PB91-103598

Emissions of Dioxins and Related Compounds from Combustion and Incineration Sources

NATO Committee on the Challenges of Modern Society, Brussels (Belgium)

Prepared for:

Environmental Protection Agency, Washington, DC

Aug 88

U.S. Department of Commerce
National Technical Information Service
NTIS

PB91-103598

Pilot Study On International Information Exchange On Dioxins and Related Compounds

Emissions of Dioxins and Related Compounds from Combustion and Incineration Sources

Report Number 172
August 1988

North Atlantic Treaty Organization
Committee on the Challenges of Modern Society

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT LATA
(Please read Instructions on the reverse before complet

1. REPORT NO. EPA/600/6 90/013	2.	3. PB91-103598
4. TITLE AND SUBTITLE Emissions of Dioxins and Related Compounds from Combustion and Incineration Sources		5. REPORT DATE August 1988 6. PERFORMING ORGANIZATION CODE NATO/CCMS
7. AUTHOR(S) O. Hutzinger and H. Fiedler		8. PERFORMING ORGANIZATION REPORT NO. CCMS Report No.172
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Bayreuth Chair of Ecological Chemistry and Geochemistry D-8580 Bayreuth Federal Republic of Germany		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Umweltbundesamt I Bismarkplatz 1000 Berlin 33 Federal Republic of Germany		13. TYPE OF REPORT AND PERIOD COVERED Final 1988 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

This report on the emissions of polychlorinated dibenzo-p-dioxins and dibenzofurens was prepared as a contribution to the Pilot Study on International Information Exchange on Dioxins and Related Compounds. The report describes the state of the art with respect to combustion and thermal processes which lead to the formation of PCDDs/PCDFs. These compounds were identified in the emissions of various combustion processes including, municipal waste incinerators, fossile fuel plants, automobiles, wood burning stoves, and PCB fires. Theoretical and experimental investigations were carried out to elucidate the formation mechanisms of PCDPs and PCDFs in combustion processes and in other high temperature processes. Although considerable progress has been made, more work is needed to eventually predict the emissions of these compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Dioxins Incineration Combustion Formation Chemistry	NATO/CCMS Pilot Study on International Information Exchange on Dioxins Emissions	
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 197
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (9-73)

TABLE OF CONTENT

Page

Table of Contents i
List of Tables iii
List of Figures x
Abbreviations xiiv
Acknowledgement xvi
Summary xvii

I. General Aspects 1

1. Introduction 1
2. Sources of Dioxins and Furans 1

II. Incineration of Solid Waste 2

1. General and Historical 2
2. Emissions and By-products of Municipal Refuse Incineration 4
   2.1 Mechanism of Dioxin and Furan Formation in Municipal Waste Incineration 4
   2.2 Survival of Dioxins and Furans in Refuse 5
   2.3 Thermal and Catalytic Reactions of Precursor Compounds 5
   2.4 Pyrolysis and Combustion Studies 5
   2.5 Formation of Dioxins via Catalytic Reactions of Precursor Compounds on Fly Ash 7
   2.6 Catalytic Formation and Decomposition of Dioxins and Furans 11
   2.7 De Novo Synthesis of Dioxins and Furans during Incineration 14
   2.8 De Novo Synthesis from Particulate Carbon 15
   2.9 Relative Importance of De Novo Synthesis and Precursor Reactions to Dioxin Formation during Incineration 21

Page

3. Incinerator Studies 24
  - 3.1 Waste Incineration in Canada 24
  - 3.2 Municipal Waste Incinerator Studies Canada, Sweden, and Germany 49
  - 3.3 Municipal Waste Incineration in Japan 65
  - 3.4 Municipal Waste Incineration in Denmark 71
  - 3.5 Municipal Waste Incineration in Sweden 74
  - 3.6 Municipal Waste Incineration in the United Kingdom and Scotland 78
  - 3.7 Resource Recovery in the United States 79
  - 3.8 Influence of the Type of Refuse 80

III. Sewage Sludge Incineration 92

IV. Hazardous Waste Incineration 95

V. Transformer And Capacitor Fires 106

VI. Combustion Of Wood 125

VII. Fossil Fuel Combustion 132

VIII. Combustion of Automobile Fuels 138

IX. PVC as Chlorine Donor 141

X. Comparison of Combustion Sources 144

References 192

LIST OF TABLES

Page

Table I: Amounts of Dioxins Produced on different Fly Ashes Using 100 μg of [$^{13}C_6$]-labelled Pentachlorophenol 8

Table II: Catalytic Dechlorination/Hydrogenation of a Mixture of 200 μg of Cl_8DD and 4 μg of Cl_8DF with 1 g of Copper at 280°C 11

Table III: Fly Ash Sample from Two Municipal Waste Incinerators and a Waste Incinerator Operated by a University 12

Table IV: Cl_8DD (2mg), Containing about 40 μg of Cl_8DF as a Contaminant, was Added to 5 g Fly Ash and Treated at 280 °C for the Time Specified 13

Table V: Thermal Behavior of PCDD on Fly Ash 16

Table VI: Thermal Behavior of PCDF in Fly Ash 16

Table VII: Formation of PCDD/PCDF 17

Table VIII: Influence of Temperature on the Formation of PCDD/PCDF 17

Table IX: Concentration of PCDD Congeners after 2 Hours of Annealing Time at 300 °C 18

Table X: Influence of Copper(II) Concentration on the Formation of PCDD/PCDF 18

Table XI: Role of Particulate Carbon on the Formation of PCDD/PCDF 19

Table XII: Formation of PCDD/PCDF on Fly Ash from Various Municipal Waste Incinerators 20

Table XIII: Performance Test Condition Selections and Settings 27

Page

Table XIV: Summary of Key Operating Parameters 27

Table XV: Summary of Key Operating Parameters (Continued) 28

Table XVI: Comparison of Emission Data 28

Table XVII: Concentrations of Organic Compounds at Boiler Inlet in Comparison to Stack 31

Table XVIII: Summary of Characterization Test Conditions 37

Table XIX: Selection of Performance Test Conditions 38

Table XX: Summary of Performance Test Conditions 38

Table XXI: Summary of Key Operating Parameters 39

Table XXII: PCDD Concentrations in Flue Gas and Efficiency of Removal 41

Table XXIII: PCDF Concentrations in Flue Gas and Efficiency of Removal 41

Table XXIV: Percent Removal of Other Organics 43

Table XXV: Proportion of Ash Collected in Each Vessel 43

Table XXVI: PCDD Concentrations in Ash 44

Table XXVII: PCDF Concentrations in Ash 44

Table XXVII: Average Parameters and Conditions of the Flue Gas Cleaning System 50

Table XXVIII: Gasphase PCDD and PCDF Removal, Run 1 51

Table XXIX: Gasphase PCDD and PCDF Removal, Run 2 51

Table XXX: Average Composition of Refuse in Two Ontario Incinerators 52

Page

Table XXXI: Concentrations of PCDD and PCDF in Refuse Samples from Two Ontario Incinerators 52

Table XXXII: Concentrations of Chlorinated Organics in Refuse Samples from Two Ontario Incinerators 53

Table XXXIII: Experiments at the Municipal Waste Incinerator in Umea, Sweden 54

Table XXXIV: Comparisons of Emission from Incineration and Related Processes in Sweden 54

Table XXXV: Quantitative Comparison of Some Selected PCDD/PCDF in Fly Ash from Different Countries 55

Table XXXVI: PCDD/PCDF-Contents in Flue Gases from Municipal Waste Combustors 57

Table XXXVII: Typical Ranges of PCDD/PCDF-Contents in Flue Gases and Residues from Municipal Waste Combustors 58

Table XXXVIII: Normal Operating Parameters of the Plant 51

Table XXXIX: PCDD-Contents in Fly Ash and Filter Dust 60

Table XL: PCDF-Contents in Fly Ash and Filter Dust 60

Table XLI: PCDD-Contents, Flue Gas 61

Table XLII: PCDF-Contents, Flue Gas 61

Table XLIII: Comparison of PCDD and PCDF Emissions during RDF-Only and RDF-Natural Gas Firing 62

Table XLIV: Comparison of 2,3,7,8,-Cl_4DD, 2,3,7,8,-Cl_4DF and Cl_4DF Emissions during RDF-Only and RDF-Natural Gas Firing 63

Table XLV: Average Emission Concentration and Emission Factors 64

Page

Table XLVI: Operating Conditions of Municipal Waste Incinerators A and B 67

Table XLVII: Analyses of Flue Gas (Exhaust Gas) 68

Table XLVIII: Analyses of Fly Ash 68

Table XLIX: Analyses of Discharged Water 69

Table L: Composition of Municipal Waste 69

Table LI: Concentrations of PCDD and PCDF in Municipal Waste Incinerators 70

Table LII: Organic Micro-pollutants in the Flue Gas Samples Operation with a Large Excess of Oxygen 76

Table LIII: Influence of Combustion Efficiency on the Production of TCDD-Equivalents 77

Table LIV: Composition of Combusted Waste 81

Table LV: Cl_4DD and Cl_4DF in the Condensate before the Abatement System (upstream) and the Stack (downstream) 81

Table LVI: Distribution of Worldwide PCDD Emissions Data (tetra through octa Congeners) 83

Table LVII: Levels of PCDD/PCDF in Precipitated Fly Ash from Municipal Waste Incinerator Plants 84

Table LVIII: Levels of PCDD/PCDF in Stack-Collected Particulates from Municipal Waste Incinerator Plants 87

Table LXIX: Levels of PCDD/PCDF in Stack Emissions from Municipal Waste Incinerator Plants 88

Table LX: Summary of Average PCDD and PCDF Congener Concentrations and Calculated Total (Cl_4-Cl_8) Values for Municipal Waste Incinerator Emissions 91

Page

Table LXI: Concentration of Chlorinated Organics in Sampling Train....93

Table LXII: Concentrations of Chlorinated Organics in Raw Sludge and Bottom Ash....94

Table LIII: Technical Parameters during Experiments 1 and 2....95

Table LIV: Incinerated Wastes....96

Table LXV: Technical Parameters during PCB-Burning Experiments....96

Table LXVI: Incinerated Wastes, Additional Wastes for Fire Sustain....97

Table LXVII: Analytical Results for Experiment 1 to 4....97

Table LXVIII: PCDD and PCDF Concentrations in Combustion Effluents from Industrial Chemical Waste Incineration....98

Table LIX: PCDDs Formed in Combustion Studies I....109

Table LX: PCDDs Formed in Combustion Studies II....109

Table LXI: PCDF Formed of "Mixture pyrolyzed Aroclor 1254 in Insulating Fluids"....114

Table LXII: PCDF Formed per Gram of Aroclor 1254 Pyrolyzed in Insulating Fluid....115

Table LXIII: Combustion of Aroclor 1254 in Insulating Fluids....116

Table LXIV: Comparison of Battelle vs. New York State Department of Health....117

Table LXV: Binghamton State Office Building. Test Plan: Measurements of Residual Contaminants....118

Table LXVI: Some Major Fires Involving PCB Transformers and Capacitors in the United States....119

Page

Table LXVII: Analysis of Fluids Involved in Transformer Fire Incidents 120

Table LXVIII: Dioxin Isomer Differentiation for Pyrolyzed HCH Residues and TCB Stillbottoms 121

Table LXIX: PCBs/PCDD/PCDF Analysis of Various Samples from the Strandley Site in Washington 122

Table LXX: Dioxin and Furan in Dust Samples from Wire Recovery Site, Pittsburgh, PA 123

Table LXXI: PCDD/PCDF Analyses (Fire in Reims); Interlaboratorial Comparison 124

Table LXXII: Sample Description 125

Table LXXIII: PCDD/PCDF from Wood Burning 126

Table LXXIV: Average Concentrations of PCDD/F in Chimney Soot [ppt] 127

Table LXXV: PCDD/PCDF Concentrations in Combustion Effluents from the Combustion of Chemically Treated Wood/Wood Products 129

Table LXXVI: PCDD/PCDF Concentrations in Combustion Effluents from the Combustion of Untreated Wood 130

Table LXXVI: Concentration of PCDD/PCDF in the Soot of Home Heating; Concentration in [ppb] 132

Table LXXVII: Average Concentrations of PCDD/F in Chimney Soot from Oil and Wood Fired Home Heating Systems 134

Table LXXVIII: PCDD/PCDF Concentrations in Effluents from Fossil Fuel Combustion 136

Table LXXIX: Total Particulate - Phase Stack Emission Concentrations of PCDD and PCDF from Two Coal-Fired Sources* 137

Page

Table LXXX: PCDD and PCDF in Car Exhausts [ng/24.8 km] 139

Table LXXXI: Analysis of PBDD/PCDF in Vehicle Exhaust 140

Table LXXXIII: Formation of PCDD/PCDF by Combustion of PVC 142

Table LXXXIV: Formation of PCDD/PCDF by Pyrolysis of PVC 143

Table LXXXV: PCDD and PCDF Released to the Environment from Combustion Sources 145

Table LXXXVI: Average Concentrations of the Toxic PCDD/PCDF-Isomers in Chimney Soot from House Heating 147

Table LXXXVII: Summary of PCDD/PCDF Stack Emissions Data from the Literature 155

Table LXXXVIII: Summary of Literature Data on PCDD and PCDF Contents of Combustion Ash 159

Table LXXXIX: Preliminary Ranked Source Category List (October 1984) 163

Table XC: Modification of Preliminary List 164

Table XCI: Final Ranked Source Category List 165

Table XCII: Summary Description of the Tier 4 Test Sites 166

Table XCIII: Mean Combustion Device Operating Parameters During the Test Runs 168

Table XCIV: Average PCDD/PCDF Outlet Emission Concentrations from the Tier 4 Test Sites (Sites Ranked by Total PCDD Concentration) 170

Table XCV: Toxic Equivalency Factors Used in Estimating 2,3,7,8-TCDD Equivalents 171

Table XCVI: Average Control Device Inlet PCDD/PCDF Emission Concentrations From the Tier 4 Test Sites (Sites Ranked by Outlet Total PCDD Concentration) 172

Page

Table XCVII: Average Outlet PCDD/PCDF Mass Emission Rates for the Tier 4 Test Sites (Sites Ranked by Total PCDD Mass Emission Rates) 173

Table XCVIII: Average Control Device Inlet PCDD/PCDF Mass Flow Rates for the Tier 4 Test Sites (Sites Ranked by Outlet Total PCDD Mass Emission Rates) 174

Table XCIX: Average Outlet Scaled PCDD/PCDF Mass Emissions for the Tier 4 Test Sites 175

Table C: Average Control Device Inlet Scaled PCDD/PCDF Mass Flow for the Tier 4 Test Sites 176

Table CI: Dioxin/Furan Precursor Data Summary 177

Table CII: Tier 4 Surrogate Measurements for Factors Affecting Dioxin Emissions 180

Table CIII: Comparison of Tier 4 Ash and Flue Gas Data 181

Table CIV: Summary of PCDD/PCDF Stack Emissions by Source Category 182

LIST OF FIGURES

Page

Figure 1: Formations of Dioxins from Pentachlorophenol on Fly Ash: Effect of Temperature 9

Figure 2: Chromatograms from GC/MS-EISIM Analyses of Labelled Dioxins Produced from Labelled Pentachlorophenol on Ontario Flyash at Two Different Flow Rates 10

Figure 3: Amount of Dioxins Formed from Carbon and Pentachlorophenol on a Model Fly Ash Consisting of 2.1% Copper(II)chloride, 2.3% C and Silica Gel at 300 °C in a Flow of Dry Air at Different Combinations of Air Flow and Heating Time 21

Figure 4: Ratios of Amounts of Dioxins Formed from Pentachlorophenol Divided by the Amounts Formed on Carbon on a Model Fly Ash 22

Figure 5: Amounts of Dioxins Formed from Pentachlorophenol on a Model Fly Ash 23

Figure 6: Process Schematic of P.E.I. Two-Stage Combustion System 25

Figure 7: Performing Testing Summary; P.E.I. Two Stage Combustion System 26

Figure 8: Stack Dioxin Homologue Distribution by Test Condition 29

Figure 9: Stack Furan Homologue Distribution by Test Condition 30

Figure 10: Total Dioxin/Furan Input/Output 31

Figure 11: Distribution of Dioxins/Furans in Solids 32

Figure 12: Distribution of Organics in Solids 32

Figure 13: Quebec Incinerator Schematic Cross-Section 34

Figure 14 Incinerator Gas Slip Stream Take-off Arrangement ..... 3[illegible]

Page

Figure 15: FLAKT's Dry-System 35

Figure 16: FLAKT's Wet-dry System 35

Figure 17: Parameters Measured during Characterization Testing 36

Figure 18: PCDD and PCDF Concentrations in Flue Gas 42

Figure 19: PCDD and PCDF Concentrations in Hopper Ashes 44

Figure 20: PCDD Homologue Distribution in Hopper Ashes 45

Figure 21: PCDF Homologue Distribution in Hopper Ashes 46

Figure 22: Concentrations of Chlorobenzenes, Chlorophenols, Polychlorinated Biphenyls, and Polycyclic Aromatic Hydrocarbons in Hopper Ashes 47

Figure 23: Municipal Waste Incinerator with Spray Absorption by Rotary Atomizer 49

Figure 24: Flue Gas Sampling System 50

Figure 25: GC/MS/SIM Showing the Isomer Distribution Pattern of Some Selected PCDD and PCDF in the Fly Ash Samples Collected from Different Countries 56

Figure 26: PCDD/PCDF in Exhaust Gas and in Fly Ashes 66

Figure 27: PCDD in Flue Gas; Comparison of Two Years 69

Figure 28: Ratio of Biphenyl, Carbon Monoxide, and PCDD after Thermal Treatment 71

Figure 29: PCDD and PCDF Concentrations as Function of Burn-out Temperature 72

Figure 30: Relationship between PCDD-and CO-Concentration for Three Incinerators 72

Page

Figure 31: Cl_5DFs in Emissions from Two Different Municipal Waste Incinerators 74

Figure 32: Congener Profile of PCDD and PCDF in Emissions from Three Swedish Municipal Waste Incinerators 75

Figure 33: Flow Diagram of Liquid PCB Waste Incineration System 100

Figure 34: Levels of Combustion Products Found in Activated Carbon 101

Figure 35: PCDF Formation in Mineral Oil by Homolog 107

Figure 36: Average PCDF Formation Versus PCB Concentration 107

Figure 37: PCDF Formation from PCB Askarel and Trichlorobenzene Fluid 108

Figure 38: Thermal Combustion System to Model PCB Fire Conditions 110

Figure 39: Comparison of PCDD and PCDF Formation from PCB, Trichlorobenzene, and Tetrachloroethylene Feeds 111

Figure 40: PCDF Formation from Aroclor 1254 in Silicone Oil by Homolog 112

Figure 41: PCDF Formation from Trichlorobenzene Feed and Tetrachloroethylene Feed 112

Figure 42: Average PCDF Formation Versus PCB Concentration 113

Figure 43: Sewage Sludge Incinerators Inlet 183

Figure 44: Sewage Sludge Incinerators Outlet 184

Figure 45: Black Liquor Boilers/Inlet 185

Figure 46: Black Liquor Boilers/Outlet 186

Figure 47: Wood Combustion/Inlet 187

Page

Figure 48: Wood Combustion/Outlet 188

Figure 49: Miscellaneous Combustion Sources/Inlet 189

Figure 50: Miscellaneous Combustion Sources/Outlet 190

Figure 51: Metals Recovery Processes/Outlet 191

ABBREVIATIONS

CB	Chlorobenzenes
Cl_xDD *	Polychlorinated dibenzo-p-dioxins (x = number of chlorine atoms in the molecule)
Cl_xDF *	Polychlorinated dibenzodioxins (x = number of chlorine atoms in the molecule)
CP	Chlorobenzene, Chlorophenols
CP	Chlorophenols
DBE	Dibromoethane
DCE	Dichloroethane
HCH	Hexachlorocyclohexane
PAH	Polynuclear aromatic hydrocarbons
PBDD	Polybrominated dibenzo-p-dioxins
PBDF	Polybrominated dibenzofurans
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
PU	Polyurethane
PVC	Polyvinyl chloride
TCB	Trichlorobenzene
TCDD	Tetrachlorodibenzo-p-dioxin
THC	Total hydrocarbon
TOX	Total organic halogen
BH_{out}	Baghouse (outlet)
CE	Combustion efficiency
CRF	Carbon Regeneration Furnace
DBR	Drum and Barrel Reclamation Incinerator
EFW	Energy-from-waste
F.F.	Fabric filter
EISIM	Electron impact single ion mode (GC/MS detection)
ISW	Industrial Solid Waste Incinerator
LR	Low Recovery
MSW	Municipal sewage waste
RDF	Refused-derived fuel
WB	Wood burning
WRI	Wire Reclamation Incinerator

AB	Afterburner
BLB	Black Liquor Boiler
CA	Chimney ash
ESP	Electrostatic precipitator
FA	Fly ash
FG	Flue gas
FP	Fire place
NITEP	National Incineration Testing and Evaluation Program
OA	Open air
SCR	Scrubber
SD	Spray dryer
SSI	Sewage Sludge Incinerator
WFB	Wood Fired Boiler
WS	Woodstove
BGA	German Federal Health Office
GefStoff	German statuatory regulation for dangerous substances
TE	Toxic equivalents
TEF	Toxic equivalents factor
ASME	American Society of Mechanical Engineers
BSOB	Binghamton State Office Building
EPA	Environmental Protection Agency (USA)
EPS	Environmental Protection Service (Canada)
FRG	German Republic of Germany
NYSDOH	New York State Department of Health
P.E.I.	Prince Edward Island
UBA	German Federal Environmental Protection Office
ppm	Parts per million
ppb	Parts per billion
ppt	Parts per trillion
NA	Not available
ND	Not detected
NS	Not sampled

---

* Abbreviations according to Fiedler and Hutzinger, 1987

ACKNOWLEDGEMENT

This report of the NATO/CCMS Pilot Study on International Information Exchange on Dioxins and Related Compounds was prepared by the University of Bayreuth. Dr. Heinrich W. Kraus, from the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Federal Republic of Germany, was the Study Director for the Technology Assessment Working Group. The principal authors of this report were Prof. Dr. Otto Hutzinger and Dr. Heidelore Fiedler, Chair of Ecological Chemistry and Geochemistry, University of Bayreuth, FRG. We would like to thank Mr. Thomas Thompson, Department of Chemistry, University of Waterloo, Ontario, Canada, for assistance in writing the report, Prof. Dr. Frank W. Karasek, Department of Chemistry, University of Waterloo, for technical advice, and Dr. Leslie C. Dickson (present address: Chair of Ecological Chemistry and Geochemistry, University of Bayreuth, FRG) for writing the Chapter on Emissions and By-products of Municipal Waste Incineration. We would also like to thank Dr. Heinz Thoma, Chair of Ecological Chemistry and Geochemistry, University of Bayreuth, for helpful discussions.

Information contained in this report was collected through contributions of:

Dr. Ray E. Clement, Ministry of the Environment, Dioxin/Mass Spec. Research, Rexdale, Ontario, Canada;

Mr. D.J. Hay, Chief, Urban Activities Division, Environmental Protection Service, Environment Canada, Ottawa, Ontario;

Professor Dr. H. Hagenmaier, Organische Chemie, Universität Tübingen, FRG;

Dr. Ludwig Stieglitz, Institut für Heiße Chemie, Kernforschungsanlage Karlsruhe, FRG;

Mrs. Connie Moller, Ministry of the Environment, National Agency of Environmental Protection, Copenhagen, Denmark;

Mr. J.J.M. Post, MT-TNO, Appeldoorn, The Netherlands;

Drs. A.A. Sein, Rijksinstituut voor volksgezondheid en milieuhygiene, Bilthoven, The Netherlands.

SUMMARY

The purpose of this report is to summarize information about PCDD/PCDF formation from combustion sources. Although progress is being made in this field not all answers are at hand.

Polychlorinated dibenzodioxins and dibenzofurans are considered ubiquituous in technologically advanced countries and combustion processes are considered one main source. PCDD/PCDF and related compounds were found in the emissions of various combustion processes: municipal and hazardous waste incinerators, fossil fuels power plants, automobile exhaust, private heating, wood and forest fires, cigarette smoking as well as accidents like PVC or PCB fires.

Even though several theoretical and experimental investigations have been carried out to elucidate the formation mechanism of PCDD/PCDF, many questions still remain unanswered; e.g. the point when chlorine or oxygen are introduced into the molecule. Furthermore, there are uncertainties, whether all combustion processes lead to PCDD/PCDF and what type of catalytic effects are important. It is likely that several mechanisms will lead to the formation of PCDD/PCDF or their precursors. The exact mechanisms involved in dioxin formation remain unclear. It is generally accepted, that thermal reactions involving direct precursors like PCP, PCB and polychlorinated benzenes and diphenylethers yield PCDDs/PCDFs.

The presence of PCDD/PCDF in flue gas and fly ash of municipal incinerators is universal. International comprehensive tests of municipal waste incinerators have established the following facts:

- All waste incinerators, independent of incinerator type or garbage composition, produce all of the possible 75 PCDD and 135 PCDF isomers and congeners as well as 400 other organic compounds. These compounds are detected in the emitted stack gases and are partially adsorbed to fly ash particles (ppb-ppm range).
- The exact reaction mechanism for dioxin formation from combustion processes is unknown.
- The total and relative amounts of PCDD/PCDF and other compounds vary daily and somehow depend on the incinerator operation conditions.

Because tons of plastics are discarded each year with garbage, it has long been debated whether PVC serves as a chlorine donor during municipal waste incineration. During random tests of various waste incinerators, no significant increases in fly ash dioxin concentrations were registered even when 300% more PVC than normal was added to the refuse. Nevertheless, PCDD and PCDF congeners were formed during laboratory pyrolysis of PVC. However, negligible amounts of dioxins were detected from a warehouse fire in Sweden involving 200 tons of pure PVC as well as 500 tons of plastics and other materials.

Well managed large systems for combustion of hazardous waste such as PCBs and chlorinated benzenes present no problems. 2,3,7,8-Cl_4DD could not be detected in the gaseous emissions even when PCBs (chlorine content 56-65%) are burnt; concentrations of other PCDD/PCDF were found in the low ppt-range, in smaller amounts than all threshold requirements.

The arcing and subsequent burning of an electrical transformer in a Binghamton State office building on February 5, 1981, produced the first recognized large scale case in which toxic products, PCDDs and PCDFs, were produced outside of the laboratory from the combustion of chlorinated aromatic compounds in the transformer fluid. Since the accident of Binghamton some major PCB transformer and capacitor fires have occurred within the U.S. and Europe. Of all theses fires, the Binghamton transformer fire is the only one in which PCDDs were clearly identified. The presence of chlorinated benzenes in the transformer fluid and the intense heat of the fire provided conditions similar to those in earlier laboratory studies which produced PCDDs from the pyrolysis of chlorinated benzenes.

Polychlorinated dioxins and furans can likewise occur by burning untreated wood. Recent studies have shown fairly high levels of dioxins in the soot from home furnaces heated with wood and/or coal. There is conflicting and limited data regarding PCDD/PCDF formation during the burning of fossil fuels, mostly of coal. In some investigations polychlorinated dioxins were detected in ppb-amounts. Small home heating units using oil and coal, however, consistently produce moderately high levels of PCDD/PCDF.

Polychlorinated as well as polybrominated dibenzodioxins and -furans have ben identified in the exhaust gases of cars and trucks fueled with leaded gasoline or diesel. Dibromoethane (DBE) and dichloroethane (DCE), which are added as scavengers to leaded gasoline to prevent lead deposits in engines, are likely involved in combustion mechanisms leading to dioxin formation.

Copper smelters and plants for metal recovery are to be considered separately, where cables covered with PVC are thermolyzed in the presence of e.g. copper. The levels of PCDD/PCDF (in 100 ppb to ppm-range) found in the emissions may be due to catalytic inference of the metals present. One should note, that the maximum and minimum values deviate by several orders of magnitude. Furthermore, the average fly ash concentrations of dioxins from hospital waste incineration are greater than those from municipal waste incineration. However, it is unclear if these variations depend on technical conditions or on the higher proportions of plastics typically found in hospital wastes. Initial tests regarding soil contamination in the immission area of metal recovery plants revealed that all PCDDs/PCDFs were detected with the isomer distribution characteristic for dioxins and furans from thermal sources. Based on the results of the Tier 4 study and information extracted from the literature, it can be concluded that total organic halogen (TOX) levels showed the strongest association with the total level of PCDDs and PCDFs emitted. Afterburners operating above 800 °C do not necessarily destroy all PCDDs and PCDFs since factors such as residence time and mixing are also significant.

I. GENERAL ASPECTS

1. Introduction

This report describes combustion and other thermal processes which lead to the formation and emission of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). It is not the goal of this report to give a detailed historical review of the research and studies which have been carried out in studying these processes. Instead the purpose is to update the state-of-the-art knowledge on combustion and thermal processes which lead to the formation and emission of dioxins and furans. The report is divided into two sections, the first of which is devoted to the emissions from incineration of waste material. The second section deals with the production of PCDD and PCDF from other combustion and thermal processes such as transformer fires, wood burning, and car engines.

2. Sources of Dioxins and Furans

Numerous combustion and other thermal processes lead to the formation and emission of PCDDs, PCDFs and various related compounds. Examples include the incineration of municipal and industrial wastes, fossil fuel combustion, the burning of natural materials, such as wood or straw and accidental fires involving chlorine-containing dielectric fluids (Ontario Ministry, 1985; Hutzinger et al., 1985; des Rosiers, 1986). In the United States alone millions of combustion sources which produce PCDDs and PCDFs (Brenner, 1986). Fuels such as oil, gas, coal, and wood are burned in residential areas to produce heat. Larger commercial, institutional, and utility boilers burn fossil fuels to produce heat, steam or electricity. Incineration of municipal and industrial wastes is commonly used to reduce the volume of refuse, yield a hygienic end product and, sometimes, to recover energy. Open fires such as agricultural burning and unintentional blazes involving residential or commercial buildings as well as forest fires are further combustion sources.

II. INCINERATION OF SOLID WASTE

1 General and Historical

Urban waste is generally divided into two broad categories: municipal solid waste and hazardous, industrial or chemical waste. Incineration of municipal refuse has become an attractive alternative to the common practice of depositing garbage in landfill sites. The trend towards incineration rather than landfilling is due largely to the lack of suitable landfill sites and also to growing concern for groundwater contamination Hay et al., 1987). The concept of producing energy by burning waste has led to the design of energy-from-waste (EFW) incinerators (Cook, 1987). Canada burns 1.5 to 2 million tons of refuse per year. The U.S.A. burns about 28 million tons, only about seven percent of the total waste produced, which is about 150 million tons of municipal waste and 250 million tons of hazardous (industrial) waste. This figure which represents about 1.5 tons/year of waste per capita is the highest in the world. The practice of incineration is more widespread and older in Europe and Japan where landfill sites are scarce and where there is a greater need for energy produced by incineration. The city of Paris, France alone incinerates over 3 million tons per year. In France about 0.8 ton/year waste per capita is generated. Germany incinerates about 8 million tons of solid wastes per year in 47 incinerators. Only 16-18 million tons per year are landfilled. Japan incinerates about 50 million tons/year in 2,000 incinerators. Sweden burns about 7 million tons/year (0.7 tons/year per capita) in 25 plants. Incinerating garbage offers the advantages of reduction in the volume of solid wastes, the possibility of energy recovery, and in the case of units close to urban areas, lower transportation costs. However, the incineration of refuse, and combustion processes in general, may emit potentially hazardous substances into the environment. Public concerns over the safety of these plants and the cost of providing adequate pollution controls have limited the growth of incineration as a waste disposal technology in North America (Cook, 1987).

The first incinerator for combustion of municipal waste was built in 1876 in Great Britain. The cities of Hamburg and New York soon followed in 1896 and 1903. England had 200 units in place by 1914. North America has generally lagged behind Europe in the use of advanced incineration technology. In 1979 there were only 23 units installed in the United States, while 180 were operating in western Europe. Over 50 percent of the installed units in western Europe were designed for energy recovery as compared to the present two percent in the United States. The extensive use of refuse incineration in Europe is due to several reasons: the high cost of fossil fuels, a shortage of landfill sites, and a high level of capital funding available for post-World War II reconstruction. In the United States its acceptance was hampered by cheap landfill, stringent air pollution controls, the low cost of fossil fuels, and a negative public reaction.

There are many different incinerator designs and large variations in the types of materials burned at such facilities. Incinerators generally consist of fuel feed mechanisms, a grate, and combustion chamber, a boiler (heat exchanger), particulate collectors, gas scrubbers and a stack. Some plants incorporate a two-stage design in which the first combustion chamber operates at a lower temperature and under fuel-rich conditions to provide partial burning and fuel-gasification. Here large organic molecules are decomposed and small molecules become oxidized. The second afterburning chamber operates with excess air to burn the remaining uncombusted organic gases. Often an auxiliary burner using natural gas or oil is used to maintain temperatures above 900 °C. Most incinerators can be considered to be one of the broadly categorized types described below.

1. Mass burn
   - used for the combustion of unsorted municipal solid waste
   - usually equipped with heat recovery units (e.g. water wall)

2. Refuse derived fuel
   - accept waste in processed form
   - refuse is mechanically pre-sorted to remove non-combustibles
   - refuse may be shredded or made into pellets
   - usually equipped with heat recovery units

3. Rotary kiln
   - used for solid, slurried, pasty and liquid wastes
   - liquid wastes often used as fuel to incinerate other wastes
   - frequently equipped with heat recovery units

4. Liquid injection
   - used for the combustion of liquid wastes which can be pumped
   - sometimes equipped with heat recovery units

5. Fume incinerator
   - used to burn by-product fumes in industrial processes
   - sometimes equipped with heat recovery units.

6. Pyrolysis

The first two types of incinerators are commonly used for the combustion of municipal waste while the latter three are usually employed for hazardous or industrial waste incineration.

Municipal refuse is not an ideal fuel for incineration because its composition is neither constant nor homogeneous. The composition depends upon the location of the incinerator. The levels of plastic materials and paper products is higher in urban waste as compared to rural waste. In addition, waste composition varies on a seasonal and weekly basis (e.g. grass cuttings in summer). The fuel can be raw refuse burned without sorting or pre-treatment (mass burning) , or fuel that has been sorted for non-combustibles or treated in some way (refuse-derived fuel).

2. Emissions and By-products of Municipal Refuse Incineration

The emissions from municipal refuse incinerators include carbon dioxide, water vapor, particulate matter in the form of fly ash and bottom ash, and process water. A large number of different metals have been found in the residues and effluents from refuse incinerators. Metals such as silver, cadmium, chromium, manganese, lead, tin, and zinc are from non-combustible refuse material. In addition, organic compounds may be found in the fly and bottom ashes as well as in the process water and stack-emitted flue gases.

Since 1964, there have been reports of organic compounds identified in incinerator residues and effluents. Compounds identified include aliphatic and polynuclear aromatic hydrocarbons (PAH), substituted benzenes, carbonyl, sulfur and nitrogen compounds, and polychlorinated aromatic compounds such as dioxins and furans. Dioxins and furans were first detected in samples of stack gases and the precipitated fly ash from three incinerators in Arnhem, Amsterdam, and Alkmaar (The Netherlands) (Olie et al., 1977). By 1980 dioxins and furans had been found in many incinerators in Europe and North America. These compounds have since been detected in every municipal incinerator tested, despite their differences in design, operation, and nature of the refuse burned. Some studies have also shown that the emissions contain related chlorinated aromatics such as polychlorinated biphenyls (PCBs) and chlorinated benzenes and phenols.

2.1 Mechanism of Dioxin and Furan Formation in Municipal Waste Incinerators

The process by which dioxins and furans are formed during incineration are not well understood nor agreed upon. Three possibilities have been proposed to explain the presence of dioxins and furans in incinerator emissions (Hutzinger et al., 1985):

1. Dioxins and furans are already present in the incoming waste and are incompletely destroyed or transformed during combustion.
2. Dioxins and furans are produced from related chlorinated precursors such as PCBs, chlorinated phenols and chlorinated benzenes.
3. Dioxins and furans are formed via de novo synthesis. This is, they are formed from the pyrolysis of chemically unrelated compounds such as polyvinyl chloride (PVC) or other chlorocarbons, and/or the burning of non-chlorinated organic matter such as polystyrene, cellulose, lignin, coal, and particulate carbon in the presence of chlorine-donors.

2.2 Survival of Dioxins and Furans in Refuse

Municipal refuse may contain herbicide formulations, wood treated with chlorinated phenol preservatives, or products containing PCBs. These minor constituents could provide a source for low level dioxin and furan contamination. However, several studies have shown that dioxin and furan levels in municipal refuse are very low to undetectable (Lustenhouwer et al., 1980; Tosine et al., 1985). The levels of these compounds in incinerator emissions are much higher than can be accounted for by the dioxin and furan content of the refuse. Also, the isomer distribution of the dioxins and furans in emissions are very different from the isomer distribution in the refuse, indicating that the dioxins and furans emitted by the incinerator were formed in the combustion process.

2.3 Thermal and Catalytic Reactions of Precursor Compounds

Our present understanding of the role of precursor compounds in the formation of dioxins come from two lines of investigation. One line is the study of the pyrolysis of pure compounds such as chlorinated phenols, benzenes, diphenylethers, 2-phenoxyphenols and PCBs, and studies of the emissions of combustion processes. The second line of investigation is the study of the role of inorganic compounds and fly ash in catalyzing gas-solid phase reactions of precursor compounds.

2.4 Pyrolysis and Combustion Studies

Dioxins can be easily formed by heating chlorophenols or alkali metal chlorophenates at temperatures over 250 °C. A major byproduct of the reaction is hexachlorobenzene, formed by the dehydration of two pentachlorophenols (Sandermann et al., 1957).

Nestrick et al. heated potassium salts of di-, tri-, and tetrachlorophenols under controlled flow pyrolysis conditions at 300 °C (Nestrick et al., 1979). Twenty-two discrete tetrachlorodioxin isomers were isolated by a combined chromatographic system for use as standards. When potassium chloro- phenates are pyrolyzed at 320 °C, the chlorine substitution pattern of the reactants was visible in the products. At 440 °C the substitution patterns were lost (Zoller and Ballschmiter, 1986).

Other dioxin precursor compounds have been studied in pyrolysis experiments. Chlorinated phenol formulations often contain dimeric impurities called 2-phenoxyphenols. They are formed when the hydroxyl group of one phenol reacts with the ortho-chlorine of another chlorinated phenol to eliminate a molecule of HCl. These "pre-dioxins" can readily undergo intramolecular cyclization and ring closure to form a dioxin (Nielsson et al., 1974). Dioxins and furans have been reported from the pyrolysis and photolysis of chlorinated diphenyl ethers (Lindahl et al., 1980; Norstrom et al., 1977). The dioxins form via intramolecular cyclization through the loss of ortho-Cl_2, ortho-HCl, and ortho-H_2 (Lindahl et al., 1980).

For many years PCBs were used in electrical transformers and capacitors because of their excellent thermal stability and insulating properties. Furans have been found in the residues from fires involving PCBs (Jansson and Sundström, 1982).

Dioxins at parts-per-billion (ppb) levels have been found in the residues and emissions of residential fireplaces (Crummett, 1982; Nestrick and Lamparski, 1982; Lao et al., 1983; Clement et al., 1985). Recently chimney soot samples from home heating furnaces in Bayreuth, Germany were analyzed for dioxins and furans (Thoma, 1988b). The furnaces burned wood, coal, wood/coal, or oil. Chlorinated dioxins and furans were found in all samples. In another study, no dioxins were detected when virgin wood was burned at 750 °C in air (Sheffield, 1985). However, when HCl-saturated air was used, dioxins were produced.

The combustion of vegetable matter has also produced dioxins. Liberti burned chestnut, mimosa, fruit and vegetables and detected phenolic compounds along with dioxins (Liberti et al., 1983). The phenolics may arise from tannins which pyrolyze to give polyhydroxyphenols and phenols (Liberti and Brocco, 1982). As may be expected, dioxins were produced when leaves and wood wool impregnated with chlorophenates were burned Rappe et al., 1978). The products from the combustion of several industrial polymers were found to contain benzene, PAH, and chlorinated alkyl benzenes as the major compounds from the combustion of PVC (Hawley-Fedder, 1984). No dioxins or dioxin precursors were found.

2.5 Formation of Dioxins via Catalytic Reactions of Precursor Compounds on Fly Ash

Incinerator fly ash is composed of the inorganic constituents of refuse and adsorbed particulate carbon and organic compounds. The basic matrix of fly ash, based on the elemental composition, is that of an alumino-silicate. A typical fly ash could be composed of: 40 percent oxygen; 20 percent carbon; with 5 to 10 percent concentrations of silicon, chlorine, sulfur, and potassium; 1-5 percent concentrations of sodium, calcium, aluminum, and zinc; and less than 1 percent concentrations of lead, tin, and copper. Chlorine would be in the form of inorganic chlorides. The ratio of particulate carbon to adsorbed organic compounds is not known. The particles have specific surface areas of 2 to 4 m^2/g and average pore diameters of 7 to 15 nm (Dickson, 1987).

Fly ash is not an inert substance, rather is promotes gas-solid phase reaction on its surface (Rghie and Eiceman, 1985a). Dibenzodioxins adsorbed on the surface of fly ash readily react with HCl and NO_2 to form chlorinated and nitrated dioxins (Eiceman and Rghie, 1984; Rghie and Eiceman, 1985a; Rghie and Eiceman, 1985b). Selective adsorption of some organic compounds has been observed. Irreversible adsorption of dioxins by fly ash may be due to bond rupture and decomposition to undetected products (Rghie and Eiceman, 1985a).

The concept that surface reactions catalytically induced on the surface of fly ash produce dioxins and furans from a host of precursors would explain most of the observed and established information about dioxins and furans in municipal incinerators. Some simple experiments by Dickson confirmed that this is a basic mechanism involved in the formation of dioxins (Dickson, 1987; Dickson and Karasek, 1987; Karasek and Dickson, 1987).

The ability of fly ash from municipal refuse incinerators located in Ontario and Machida, Japan and from a copper smelter in Noranda, Quebec to catalyze the formation of dioxins and furans was probed using ^{13}C-isotopically labelled pentachlorophenol. The use of a stable isotope labelled precursor eliminated interferences from residual levels of unlabelled dioxins co-extracted from the fly ash. In separate experiments the labelled pentachlorophenol was passed through flow-tube reactors which contained one of the fly ashes at 300 °C and in which a flow of 10 ml/min of nitrogen was maintained for one hour.

GC-MS analyses of the fly ash extracts showed that $^{13}C_{12}$-chlorinated dioxins were produced from the pentachlorophenol precursor. No chlorinated furans were detected in the reaction products of any of the experiments conducted using chlorinated phenol precursors. The experiment using Ontario fly ash produced about seven times the amount of dioxins as the experiment with Machida fly ash. The amount of dioxins produced using the Noranda fly ash was less than one percent of that produced using Ontario fly ash. It was interesting to note that the distribution of congeners produced using Ontario and Machida fly ashes are very similar, despite the large difference in the total amounts produced. Only very small amounts of octachlorodioxin was detected in the experiments using ground firebrick as a control.

Table I: Amounts of Dioxins Produced on Different Fly ashes Using 100 μg of [$^{13}C_6$]-labeled Pentachlorophenol
Amounts given in [ng]; ND = Not detected
(taken from Dickson, 1987)

Fly Ash	Cl_4DD	Cl_5DD	Cl_6DD	Cl_7DD	Cl_8DD
Ontario	331	803	936	1,005	185
Machida	54	115	121	132	40
Noranda	ND	ND	ND	11	18

The results indicated that the Ontario fly ash, and to a lesser extent the Machida fly ash, promoted the production of dioxins from pentachlorophenol. Since all the fly ash and firebrick samples had similar physical characteristics, differences in surface elemental composition of the fly ashes were likely responsible for the differences in the catalytic activity. The chlorine content of Ontario and Machida fly ashes was in the range of 6.2 to 6.9 percent while it was absent in the Noranda fly ash. The surface concentration of aluminum in Ontario fly ash was greater than the other fly ashes. The surface sulfur content of the Noranda fly ash was the highest of all.

The pentachlorophenol experiments were repeated with $^{13}C_6$-phenol to determine if inorganic chlorides on the fly ash would chlorinate the aromatic ring and promote the formation of dioxins. The phenol did react with the fly ash surface to form mostly labelled tetrachlorodioxins and a trace amount of labelled pentachlorodioxin. These results tend to confirm that inorganic chlorides on the surface are involved in the reaction mechanism.

The effect of temperature on the amount and distribution of dioxins produced from pentachlorophenol on Ontario fly ash was investigated. At 150 °C only octachlorodioxin was detected, however it was present at a level too low for accurate quantitation. At 250 °C the octachlorodioxin isomer predominated. With a temperature increase of only 50 °C, large amounts of tetra-, penta-, and hexachlorinated dioxins were formed. At 340 °C the levels of dioxins decreased to approximately 25 percent of the levels at 300 °C.

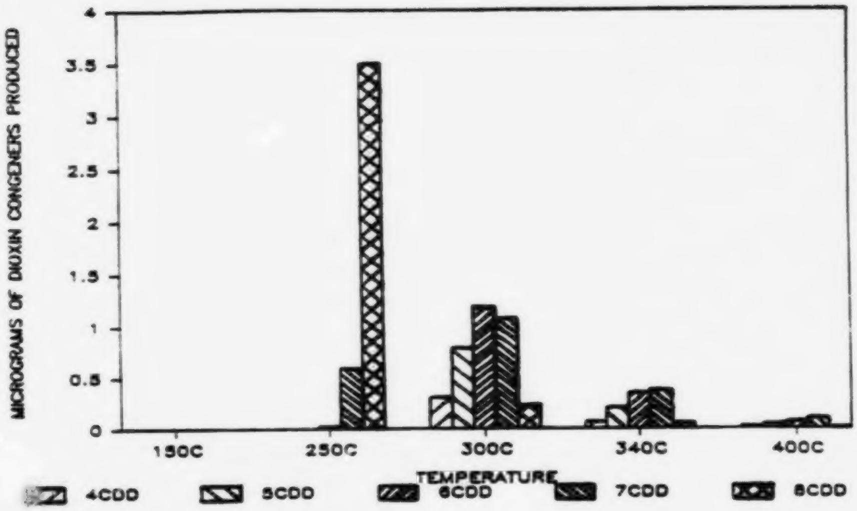


Figure 1: Formation of Dioxins from Pentachlorophenol on Fly Ash: Effect of Temperature

A change in residence time, which is dependent upon the nitrogen flow rate, changed the amounts and distribution of dioxins produced from pentachlorophenol. A shorter residence time of 9 seconds shifted the distribution of dioxins towards the higher chlorinated congeners as compared to the usual residence time of 90 seconds. The shorter residence time was insufficient to produce detectable quantities of tetra- and pentachlorodioxins.

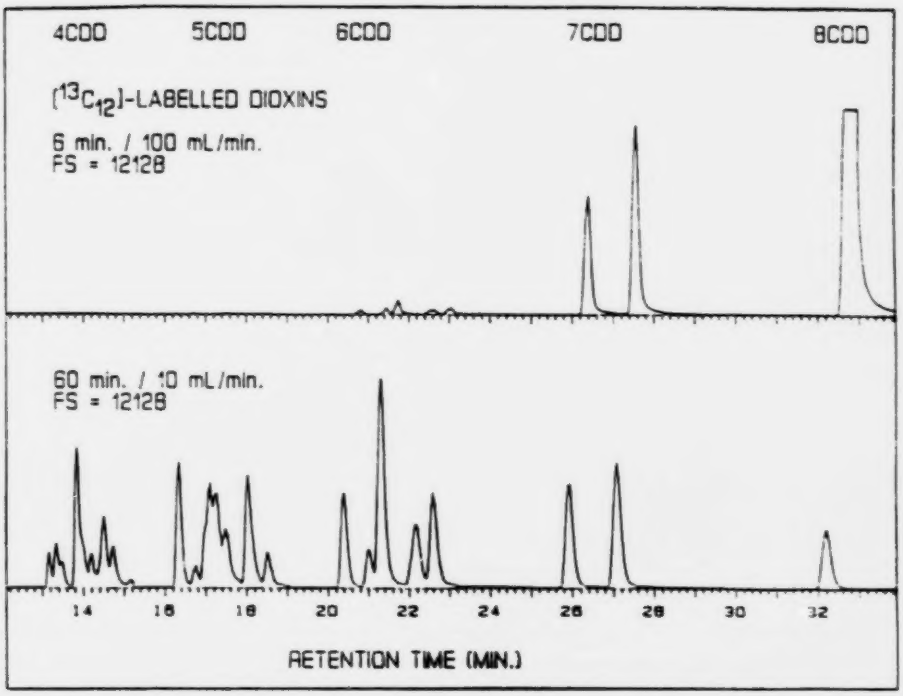


Figure 2: Chromatograms from GC/MS-EISIM Analyses of Labelled Dioxins Produced from Labelled Pentachlorophenol on Ontario Flyash at Two Different Flow Rates

Chlorinated dioxins were also produced from 2,4,5- and 3,4,5-trichlorophenol precursors. The dioxin isomer distributions were different from that produced from pentachlorophenol. The experiment with 2,4,5-trichlorophenol produced primarily hexachlorodioxins, whereas octachlorodioxin and heptachlorodioxin were the major products of the experiment with 3,4,5-trichlorophenol.

Aliquots of two solutions, one containing either selected PVC pyrolysis products (cinnamyl chloride, 2-chloro-p-xylene, and naphthalene), the other containing products of combustion of a commercial PVC formulation were passed through a reaction tube containing Ontario fly ash at 300 °C in separate experiments. In both cases dioxins were detected in the reaction products but were not detected in the starting solutions.

2.6 Catalytic Formation and Decomposition of Dioxins and Furans

Hagenmaier and co-workers have studied the catalytic effects of copper powder and fly ash on the dechlorination/hydrogenation of dioxins and furans (Hagenmaier et al., 1987a).

When 100 µg of a mixture of octachlorodioxin and octachlorofuran were heated in an open tube at 280 °C for five minutes, tetra- through heptachlorinated dioxins and furans were produced. The amount of chlorinated congener produced increased with decreasing degree of chlorination. Over 99 percent of the starting material was either decomposed or converted to the lower congeners. Only 0.15 percent of the octachlorodioxin and 0.75 percent octachlorofuran was recovered after five minutes. After 15 minutes all dioxin and furan levels were below detection limits (Table II).

Table II: Catalytic Dechlorination/Hydrogenation of a Mixture of 200 µg of Cl_8DD and 4 µg of Cl_8DF with 1 g of Copper at 280 °C

PCDD/PCDF	Heat Treatment 5 min [ng]	15 min [ng]
2,3,7,8-Cl_4DD	750	<0.1
Cl_4DDs	12,000	<0.1
Cl_5DDs	1,930	<0.1
Cl_6DDs	360	<0.1
Cl_7DDs	290	<0.1
Cl_8DDs	290	<0.1
Sum of PCDD	14,870	
Cl_4DFs	480	<0.1
Cl_5DFs	290	<0.1
Cl_6DFs	200	<0.1
Cl_7DFs	180	<0.1
Cl_8DFs	30	<0.1
Sum of PCDF	1,180	

The reactions also proceed at lower temperatures. At 150 °C tetra- through hexachlorinated dioxins and furans are found after a 5 minute heating period. After 30 minutes 80 percent of the octachlorodioxin and 60 percent of the octachlorofuran were dechlorinated to yield the lower chlorinated dioxins and furans. The dioxin was found to be slightly less stable than the furan. Octachlorodioxin could be dechlorinated in the presence of copper at a temperature as low as 120 °C.

When octachlorodioxin was heated in the presence of copper and deuterated water, deuterated tetra- through heptachlorodioxins were observed, indicating that the moisture is the likely source of the hydrogen. No interconversion of dioxins to furans or furans to dioxins was observed.

Refuse incinerator fly ash was also shown to catalyze dechlorination/hydrogenation reactions of dioxins and furans (Hagenmaier et al., 1987b). Aliquots of fly ash taken from three different refuse incinerators were heated in flasks at 280 °C for two hours.

Table III: Fly Ash Sample from Two Municipal Waste Incinerators (Fly Ash A and C) and a Waste Incinerator Operated by a University (Fly Ash B) were Heated at 280 °C for 2 hours

	Fly Ash A [ng/g]		Fly Ash B [ng/g]		Fly Ash C [ng/g]	
	untreated	280°C, 2h	untreated	280°C, 2h	untreated	280°C, 2h
2,3,7,8-Cl_4DD	0.5	0.9	2.0	3.2	0.6	1.6
Cl_4DDs	24	21	24	59	12	30
Cl_5DDs	116	13	116	88	59	29
Cl_6DDs	185	6	233	50	110	18
Cl_7DDs	159	2	1,067	22	200	15
Cl_8DDs	88	1	6,204	11	458	13
Sum of PCDD	572	49	7,644	230	839	105
Cl_4DFs	111	14	139	41	62	38
Cl_5DFs	188	12	393	69	250	41
Cl_6DFs	123	4	415	34	377	30
Cl_7DFs	35	1	844	9	292	16
Cl_8DFs	26	nd*	1,368	4	400	7
Sum of PCDF	483	31	3,159	157	1,381	132

* The PCDD/PCDF concentrations obtained are compared with those of the untreated samples.

nd = not determined.

In all cases the concentrations of all furans and penta- through octachlorodioxins decreased while the amount of tetrachlorodioxins increased. The total amounts of dioxins and furans decreased to less than 12 percent of the original levels. Similar results were obtained using sealed tubes. When a mixture of octachlorodioxin and octachlorofuran was added to a refuse incinerator fly ash sample and heated at 280 °C for 15 minutes, approximately 99 percent of the added octachlorodioxin disappeared and high concentrations of lower chlorinated dioxins were formed Table IV). Mono- through heptachlorodioxins accounted for 70 percent of the dechlorinated octachlorodioxin. After 2 hours most of the dioxins had disappeared. Fly ash treated with hydrochloric acid to remove the heavy metals present in the ash did not catalyze the dechlorination of octachlorodioxin or furan, indicating that metals present in the fly ash may be the catalytic agents for dechlorination/hydrogenation.

Table IV: Cl_8DD (2 mg), Containing about 40 µg of Cl_8DF as a Contaminant, was Added to 5 g Fly Ash and Treated at 280 °C for the Time Specified

	280 °C for 15 min, [ng/g]	280 °C for 2 h, [ng/g]
Cl_4DDs	52,000	12,900
Cl_5DDs	82,500	2,600
Cl_6DDs	23,700	470
Cl_7DDs	9,300	210
Cl_8DDs	3,700	170
Sum of PCDD	174,100	17,850
Cl_4DFs	1,400	620
Cl_5DFs	3,100	150
Cl_6DFs	840	< 1
Cl_7DFs	230	< 1
Cl_8DFs	23	< 1
Sum of PCDF	5,593	770

*The PCDD/PCDF concentrations are expressed as ng/g of fly ash.

Fly ash taken from a hospital incinerator was not as effective a dechlorination catalyst as fly ash taken from municipal refuse incinerators. However, the concentrations of dioxins and furans in the untreated fly ash from the hospital incinerator were considerably higher than those observed for the municipal refuse incinerator fly ash. The researchers suggest that this difference may be due to the higher percentage of plastic and lower percentage of metals in the waste feed.

When fly ash from a municipal incinerator was heated in a stream of air the levels of dioxins and furans increased. The levels decreased when the fly ash was heated in a stream of nitrogen or in a sealed tube. The addition of HCl to the air stream increased the levels of dioxins and furans over that of air alone, and favoured the production of the higher chlorinated isomers. This suggests that chlorine formation may be involved in the production of dioxins and furans on fly ash. Fly ash heated in a stream of air and subsequently in a sealed tube was found to produce a significant quantity of dioxins and furans. The catalytic activity of the fly ash was suggested to have decreased during the heating in air resulting in a slower rate of dechlorination. The experiment appeared to favour the production of lower chlorinated dioxins and furans.

In order to investigate the role of precursors in the formation of dioxins and furans during the heating of fly ash, a simple experiment was performed. Fly ash was heated in a sealed tube in order to eliminate dioxins and furans as well as precursors through dechlorination. After treatment the fly ash was heated in a stream of air. Increased levels of dioxins and furans were found in the treated fly ash which implies that they were formed via de novo synthesis and not from precursor originally present in the fly ash. This de novo synthesis may involve metal chlorides present in the fly ash matrix.

2.7 De Novo Synthesis of Dioxins and Furans during Incineration

Some studies have provided evidence for the possibility for the formation of dioxins and furans from reactions of chemically dissimilar compounds and sources of chlorine. Bituminous coal, when oxidized at high temperature in the presence of a source of chlorine, does produce dioxins. The best yields of dioxins were obtained using HCl or Cl_2 in air (Mahle and Wittig, 1980). Phenol and HCl reacted to produce dioxins when heated in a sealed quartz tube at high temperature (Eklund et al., 1986). The reaction was pH dependent, with the yield of dioxins dependent upon HCl concentration. Chlorinated benzenes are also important intermediates which can thermally react to form PCBs and chlorinated furans (Choudhry and Hutzinger, 1983).

Some of these chlorinated compounds can be produced from very simple molecules. Burning methane with dichloromethane produced chlorinated and non-chlorinated PAH. When fuel was enriched with HCl, no chlorinated organics were detected (Krishnan and Hites, 1980). Natural processes such as forest fires can produce chlorinated organics in the presence of chlorine-containing minerals (Palmer, 1976).

The de novo synthesis of dioxins formed the basis of a study conducted in the late 1970s which reached the conclusion that dioxins are ubituitous in the environment Bumb et al., 1980; Crummett and Townsend, 1984)). The theory advanced as the "trace chemistry of fire" was used to explain the presence of dioxins and related compounds in refuse incinerators, fossil fuel power-plants gasoline and diesel-powered vehicles, fireplaces, charcoal grills, and cigarettes. This hypothesis stated that dioxins could be formed as a result of reactions of compound at very low concentrations or from very low yield reactions of more concentrated compounds. The reactions involved were not well defined.

2.8 De Novo Synthesis from Particulate Carbon

Vogg and Stieglitz have established that particulate carbon can react with oxygen and inorganic chlorides, with copper (II) as a possible catalyst, to form organochlorine compounds, including dioxins and furans (Vogg and Stieglitz, 1986; Stieglitz and Vogg, 1987; Vogg et al., 1987; Stieglitz et al., 1987). The researchers have concluded that this de novo synthesis of organohalogen compounds is the primary source of dioxins and furans produced during MSW incineration (Stieglitz et al., 1987).

The researchers noted that when fly ash was heated in a stream of air the dioxin and furan content increased (Vogg and Stieglitz, 1986). The maximum increase was at temperatures in the range of 250 °C to 350 °C. With increasing temperature the concentration maximum shifted to lower chlorinated congeners. At 500 °C decomposition occured, and nearly complete degradation was noted at 600 °C after several hours.

Table V: Thermal Behaviour of PCDD on Fly Ash [ng/g fly ash]

	non treated	Temperature [°C]					
		120	200	300	400	500	600
A. Fly Ash							
Cl$_8$DD	120	120	90	640	6	0.2	0.1
Cl$_7$DD	125	90	100	1,000	15	0.2	0.1
Cl$_6$DD	85	65	65	1,640	22	1.	0.1
Cl$_5$DD	45	35	40	570	35	1.	0.1
Cl$_4$DD	20	15	15	65	13	2.	0.1
Sum (solid)	395	325	310	3,915	91	4.4	0.1
B. Gas Phase							
Cl$_8$DD	-	-	-	0.2	9	0.3	0.1
Cl$_7$DD	-	-	-	0.4	45	0.8	0.1
Cl$_6$DD	-	-	-	0.8	88	2.	0.1
Cl$_5$DD	-	-	-	0.15	100	3.	0.1
Cl$_4$DD	-	-	-	0.1	37	3.	0.1
Sum (vaporized)	-	-	-	1.6	280	9.	0.1
Total Sum (A+B)	395	325	310	3,916	370	13.5	0.1

Tab. VI: Thermal Behaviour of PCDF in Fly Ash [ng/g fly ash]

	non treated	Temperature [°C]					
		120	200	300	400	500	600
A. Fly Ash							
Cl$_8$DD	12	11	12	218	4	0.1	0.04
Cl$_7$DD	48	42	48	1,030	37	0.4	0.1
Cl$_6$DD	56	51	61	1,253	80	1.4	0.1
Cl$_5$DD	129	119	129	1,570	187	8.	0.2
Cl$_4$DD	113	95	122	506	140	8.	0.1
Sum (solid)	358	318	372	4,577	448	18	0.4
B. Gas Phase							
Cl$_8$DD	-	-	-	0.2	8	1.5	0.1
Cl$_7$DD	-	-	-	0.4	75	15	1.
Cl$_6$DD	-	-	-	0.8	180	34.	2.
Cl$_5$DD	-	-	-	0.15	500	93.	9.
Cl$_4$DD	-	-	-	0.1	390	95.	15.
Sum (vaporized)	-	-	-	4.	1,151	238.	27.
Total Sum (A+B)	358	318	372	4,581	1,601	256.5	27.5

Further studies showed that the presence of oxygen and ions of transition or heavy metals were necessary for a concentration increase to take place (Stieglitz and Vogg, 1987). Decreases in the carbon content of the fly ashes upon heating led to the assumption that particulate organic carbon may be involved in dioxin and furan formation (Stieglitz et al., 1987).

Table VII: Formation of PCDD/PCDF
(System: Fly ash with 1% active charcoal, 1% potassium chloride and 0.4% copper(II); 2 hours at 300 °C)

Cl_4DD	215 [ng/g]	Cl_4DF	715 [ng/g]
Cl_5DD	879 [ng/g]	Cl_5DF	3,876 [ng/g]
Cl_6DD	2,406 [ng/g]	Cl_6DF	2,958 [ng/g]
Cl_7DD	2,440 [ng/g]	Cl_7CF	2,904 [ng/g]
Cl_8DD	1,435 [ng/g]	Cl_8DF	1,204 [ng/g]
Total PCDD	7,375 [ng/g]	Total PCDF	11,660 [ng/g]

Experiments with model mixtures of carbon-free fly ash or of magnesium-aluminum-silicate with particulate carbon, potassium chloride and metal chlorides showed that at 300 °C in an air stream considerable amount of dioxins and furans can be produced (Stieglitz et al., 1987) (Table VIII).

Table VIII: Influence of Temperature on the Formation of PCDD/PCDF

	250 °C	300 °C	350 °C
PCDD [ng/g]	18.6	1,060	15.5
PCDF [ng/g]	65	5,337	126

The yields depended upon the reaction time, concentration and nature of the particulate carbon, and the presence of water vapor. A minimum of two hours was necessary to produce detectable levels of dioxins and furans (Table IX).

Table IX: Concentration of PCDD Congeners after 2 hours of Annealing Time at 300 °C (System: Mg-Al-silicate, 4% charcoal, 3% chloride, 0.4% Cu(II); 300 °C)

Cl_8DD	10,000 [ng/g]
Cl_7DD	7,300 [ng/g]
Cl_6DD	2,000 [ng/g]
Cl_5D	80 [ng/g]
Cl_4D	50 [ng/g]

Of a large number of metal chlorides tested, only copper (II) chloride resulted in dioxin and furan formation. Yields were proportional to copper concentration. The chemistry is not clearly understood, but two processes are likely involved: the production of elemental chlorine from reactions between inorganic chlorides and oxygen (the Deacon reaction) and copper-catalyzed radical formation.

Table X: Influence of Copper(II) Concentration on the Formation of PCDD/PCDF (System: Mg-Al-silicate, 1% charcoal, 1% KCl, heated at 300 °C, 2 hours) in Air Stream; (150 mg H_2O/l)

	PCDD/PCDF Concentrations [ng/g] Percent Cu^{2+} added			
Congener	0	0.08	0.24	0.4
Cl_4DD	1.3	8	20	13
Cl_5DD	1.0	20	80	65
Cl_6DD	0.9	37	240	400
Cl_7DD	0.3	24	230	860
Cl_8DD	1.0	12	200	110
PCDD	4.50	101	770	1,448
Cl_4DF	7	100	310	260
Cl_5DF	11	310	1,290	1,550
Cl_6DF	3	230	1,150	3,100
Cl_7DF	1.6	100	690	2,730
Cl_8DF	0.07	20	200	840
PCDF	22.6	760	3,640	8,480

Only negligible levels of dioxins and furans were produced using graphite, while large amounts of dioxins and furans were produced using sugarcoal, charcoal, domestic soot. The authors speculated that the crystalline lattice of graphite resisted attack by chlorine and oxygen much more than the other types of carbon which are composed of degenerated graphitic structures.

Table XI: Role of Particulate Carbon on the Formation of PCDD/PCDF

Origin of carbon	PCDD [ng/g]	PCDF [ng/g]
Soot *	212	
Sugar coal **	944	5,050
Charcoal ***	2,439	7,750
Graphite ****	0.3-0.5	0.3-0.5

* from a domestic oil burner, purified by extraction with methylene chloride and thermal treatment at 500 °C (5 hrs.) in vacuum

** obtained by pyrolysis of glucose and conditioning with CO_2 at 800 °C

*** active charcoal, purified by extraction with methylene chloride (15 hrs.) and vacuum drying at 500 °C (2 hrs.)

**** purified as described for soot.

The authors postulated that the reactions found in the laboratory experiments occur in a similar way also in the incinerator and are a pathway for dioxin and furan formation. This hypothesis might explain the simultaneous production of a variety of different chlorinated compounds which have been identified in the emission of municipal solid waste incinerators.

Table XII: Formation of PCDD/PCDF on Fly Ash from Various Municipal Waste Incinerators
(300 °C, 2 hrs., carrier gas: air)

		Concentrations in [ng/g]			
		Dioxins		Furans	
	# Chlorine	untreated	after annealing	untreated	after annealing
Plant A	Cl_8	120	640	12	218
	Cl_7	125	1,000	48	1,030
	Cl_6	85	1,640	50	1,250
	Cl_5	45	570	130	1,570
	Cl_4	20	65	110	500
Plant B	Cl_8	160	280	40	70
	Cl_7	50	360	60	230
	Cl_6	24	310	30	250
	Cl_5	10	170	20	240
	Cl_4	3	50	3	180
Plant C	Cl_8	23	330	3	240
	Cl_7	18	530	11	520
	Cl_6	13	360	14	450
	Cl_5	6	180	30	500
	Cl_4	5	30	14	220

2.9 Relative Importance of De Novo Synthesis and Precursor Reactions to Dioxin Formation during Incineration

A recent study by Dickson investigated the relative importance of dioxin and furan formation via de novo synthesis and formation via reactions of precursors on fly ash (Dickson et al., 1988). Model fly ash mixtures containing silica gel, activated charcoal, copper (II) chloride, and ^{13}C-labelled pentachlorophenol were heated at 300 °C in flow-tube reactors at four combinations of heating time and air flow rate. The levels of dioxins produced from pentachlorophenol were very much higher than those produced via de novo synthesis from carbon. Yields from both processes were strongly influenced by flow rate and heating time, however tha two processes were affected differently. The levels of dioxins formed from pentachlorophenol were about 400,000 times higher than those formed from carbon at an air flow rate of 3.2 ml/minute for a heating time of 10 minutes. At 19 ml/minute and 60 minutes heating time the levels of dioxins from pentachlorophenol were 10,000 times higher than those produced from carbon.

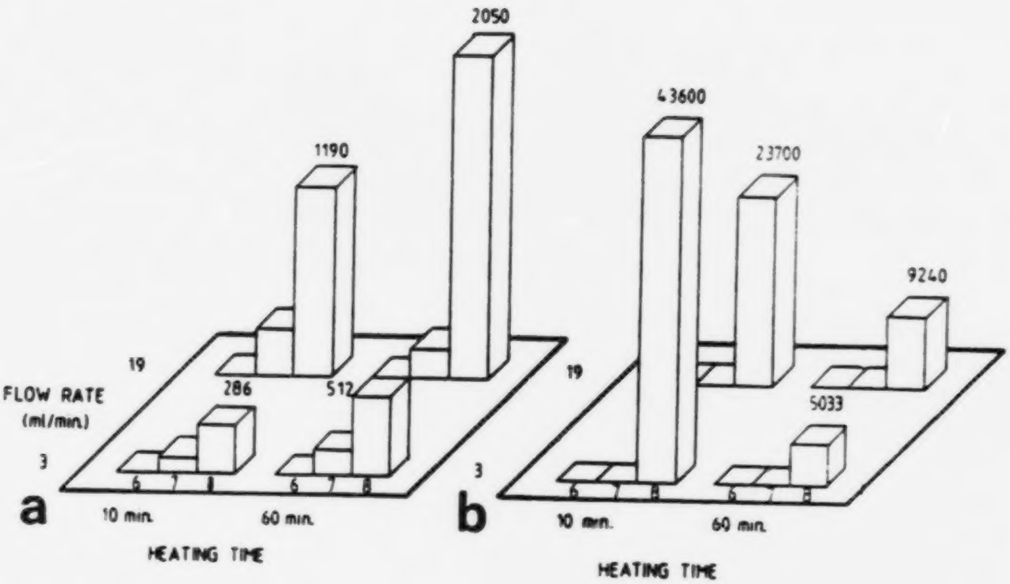


Figure 3: Amount of Dioxins [ng] Formed from Carbon (a) and Pentachlorophenol (b) on a Model Fly Ash Consisting of 2.1% Copper(II)chloride, 2.3% C and Silica Gel at 300 °C in a Flow of Dry Air at Different Combinations of Air Flow and Heating Time

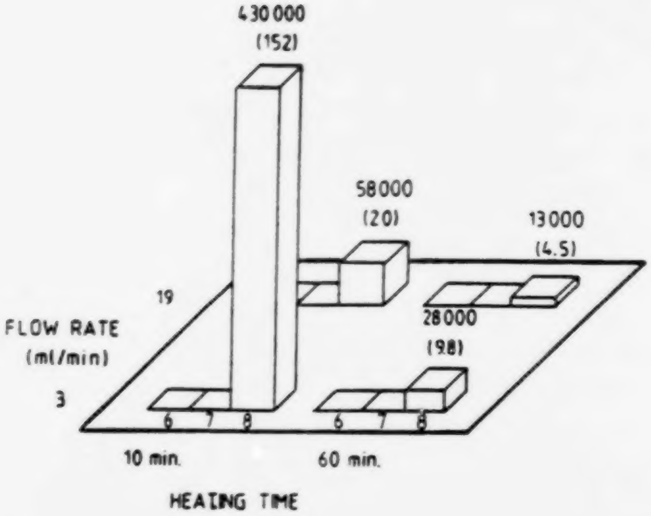


Figure 4: Ratios of Amounts of Dioxins Formed from Pentachlorophenol divided by the Amounts Formed on Carbon on a Model Fly Ash Consisting of 2.1% Copper(II)chloride, 2.3% Carbon and Silica Gel at 300 °C in a Flow of Dry Air at Different Combinations of Air Flow and Heating Time.
(The measured data are indicated in brackets, the values above are normalized for the molar ratio of carbon to pentachlorophenol)

Dioxins were also formed in large amounts from pentachlorophenol on a mixture which did not contain copper (II) chloride. The authors concluded that the carbon acted as a catalyst for the formation of dioxins from pentachlorophenol. The function of copper(II)chloride therefore may be to catalyze the dechlorination of dioxins, rather than catalyzing the initial formation of dioxins.

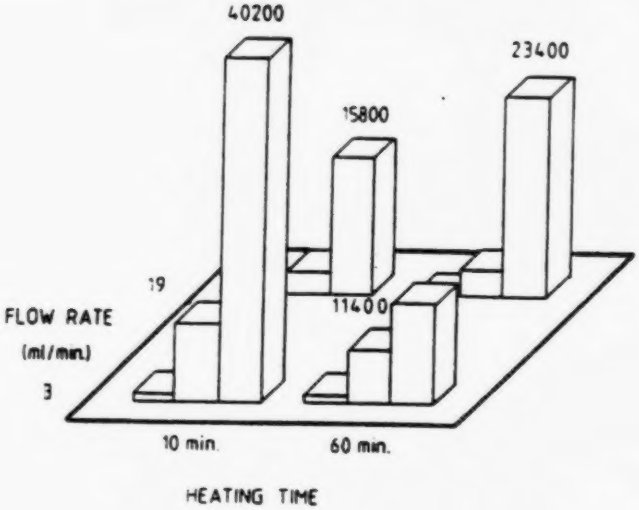


Figure 5: Amounts of Dioxins [ng] Formed from Pentachlorophenol on a Model Fly Ash Consisting of 2.3% Carbon and Silica Gel at 300 °C in a Flow of Dry Air at Different Combinations of Air Flow and Heating Time

3. Incinerator Studies

3.1 Waste Incineration in Canada

Environment Canada established the National Incinerator Testing and Evaluation Program (NITEP) (EPA Canada, 1985) in order to:

1. Find optimum design and operating parameters for municipal incinerators to minimize emissions of substances of environmental concern
2. Relate operating conditions to the emissions observed for each incinerator design
3. Investigate alternative combustion and emission control technologies for the determination of the best practical incinerator operation
4. Provide design and operating guidelines for future incinerators
5. Develop internationally recognized protocols for the sampling and analysis of PCDDs, PCDFs, and other emission pollutants
6. Determine if surrogates exist for PCDDs which can be readily and inexpensively monitored as indicators for PCDD emission levels.

NITEP planned to study three generic types of municipal incinerators:

1. Two-stage combustion system
2. Mass burning system
3. Prepared burning system

The results of a comprehensive study of the first incinerator design were published in a report released in 1985 (EPS Canada, 1985).

The two-stage incinerator is illustrated and briefly described in Figure 6. The test program carried out on this facility was one of the most extensive ever performed. The first phase characterized the key operational variables for the incinerator. The characteristics studied in the performance testing are summarized in Figure 7. Based on the initial studies, four specific test conditions were chosen for the extensive performance assessment. The rationale behind the choice of the particular test conditions is summarized in Table XIII. These tests were performed in triplicate. Individual control readings taken for triplicate test runs showed that consistent operational control was achieved. The key operating parameters for the four test conditions are listed in Tables XIV and XV.

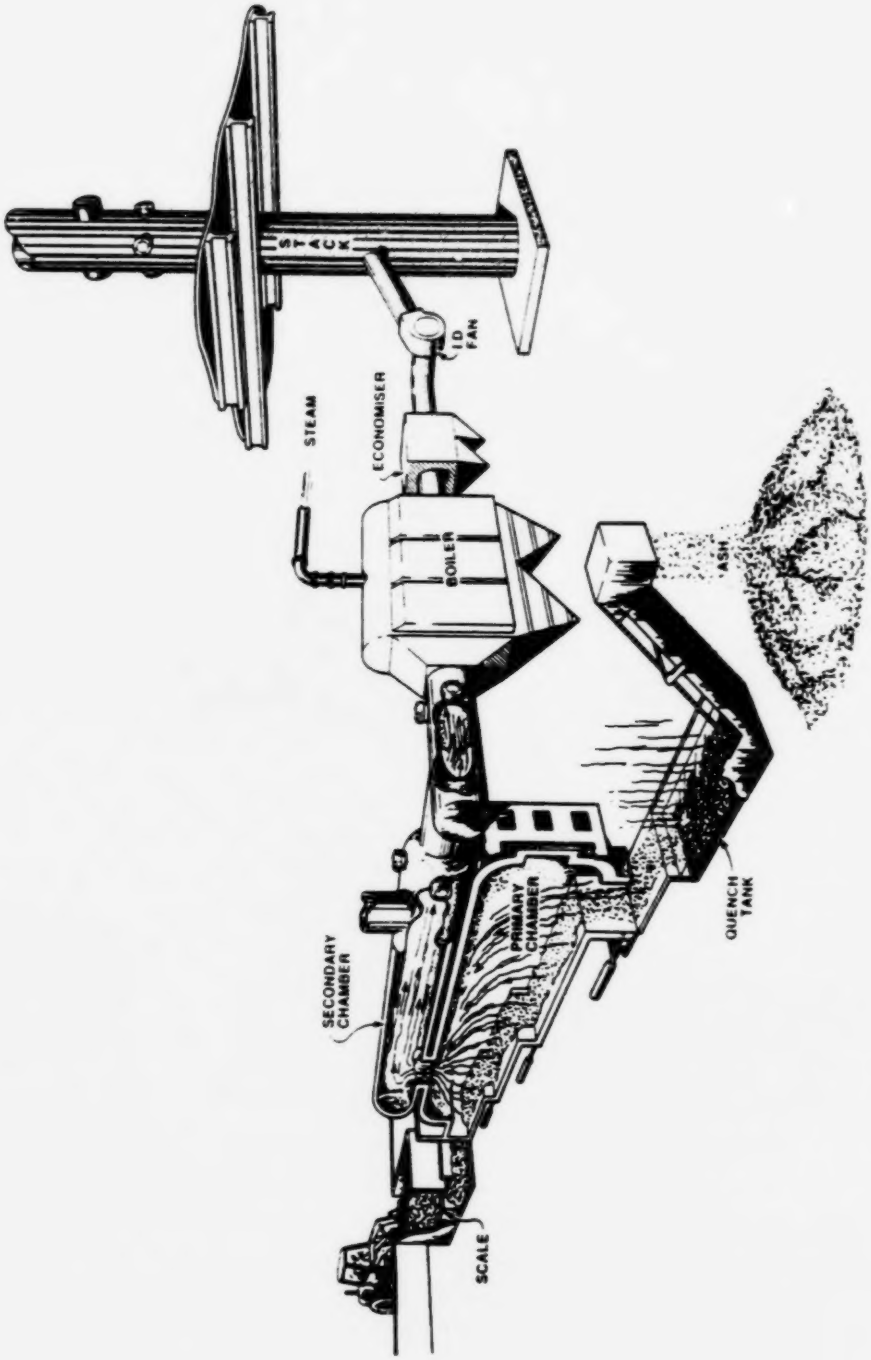


Figure 6: Process Schematic of P.E.I. Two-Stage Combustion System

Reproduced from best available copy.

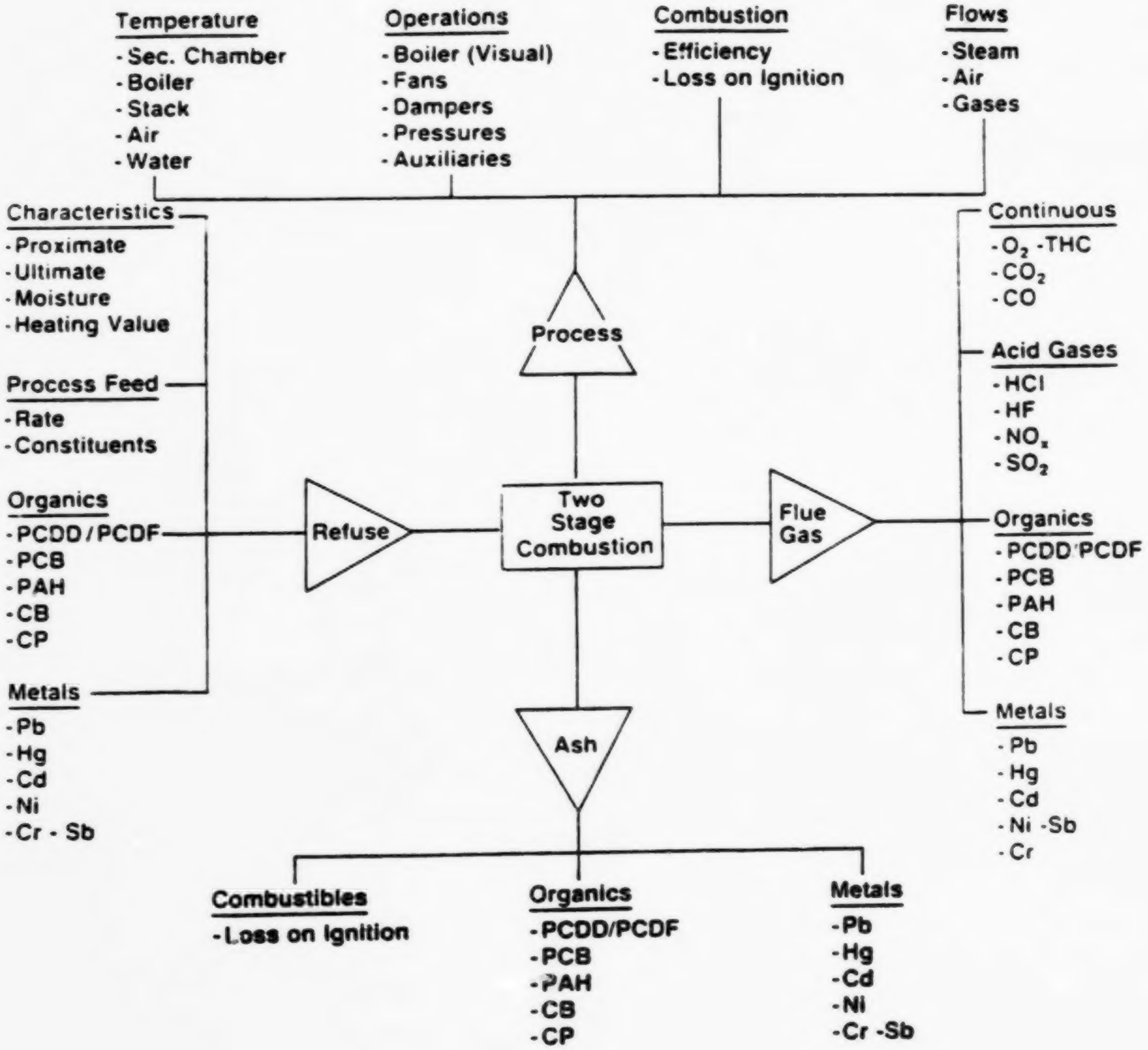


Figure 7: Performing Testing Summary; P.E.I. Two Stage Combustion System

Table XIII: Performance Test Condition Selections and Settings

Condition	Settings Primary Temp. °C	 Secondary Temp. °C*	 Feed Cycle Min.	Rationale
Normal Operation	700	1000	8.7	Benchmark for comparison with other tests
Long Feed Cycle	700	1000	12.5	Observed improvements in performance and reduced demands on plant loader operator
High Secondary Temperature	700	1135	8.7	To determine influence of high temperature on organic emissions such as dioxins and furans
Low Secondary Temperature	700	900	8.7	To investigate a condition which was thought to create higher organic emissions

Table XIV: Summary of Key Operating Parameters I

Operating Conditions	Normal Condition	Long Cycle	High Secondary Temperature	Low Secondary Temperature
Primary Temperature (°C)	695	690	703	676
Secondary Temperature (°C)	910	890	1080	780
Steam Rate (kg/h)	4360	4020	4470	3960
Refuse - Rate (kg/h wet)	1590	1600	1700	1520
- Calorific Value (kJ/kg as fired)	10 530	10 220	10 430	10 770
- Moisture (%)	35	35	32	35
- Non-combustibles (% wet basis)	14.0	13.9	15.0	13.0
Energy Input (kJ/h) x 10^6	16.8	16.2	17.6	16.0
Efficiency (%) - Input/Output	59.6	56.6	58.4	55.9
- Heat Loss	52.0	50.9	58.1	50.7

Table XV: Summary of Key Operating Parameters II

Operating Description	% CO_2	% O_2	% Excess Air
Normal Condition	8	12	140
Long Cycle	8	12	145
High Secondary Temperature	10	10	85
Low Secondary Temperature	7	13	185

The stack emissions (corrected to 12% CO_2) averaged for the triplicate tests of each condition are shown in Table XVI. From this data it is apparent that organic emission rate is generally higher at the lower secondary chamber temperature. The emission rate for metals, however, appears to be affected in just the opposite manner (i.e. decreases with decreasing temperature). Therefore there is a conflict of environmental impact interests. The amount of PCDDs emitted appears to increase with decreasing secondary chamber temperature whereas the PCDF emission is lower at both the higher and lower operating temperatures than at the normal conditions. The latter result is particularly puzzling and no explanation was proposed.

Table XVI: Comparison of Emission Data

	Stack Concentration (at 12% CO_2) Dry			
Contaminant	Normal	Long	High	Low
TSP (mg/Nm^3)	208	230	247	167
HCl (mg/Nm^3)	1 085•	1 070	1 165	950
PCDD (ng/Nm^3)	107	107	62	123
PCDF (ng/Nm^3)	143	156	95	98
PCB (ng/Nm^3)	801	58	ND	126•
PAH (ng/Nm^3)	7 005	8 010	6 653	12 490•
Chlorophenol (ng/Nm^3)	4 346	3 773	2 706	6 591•
Chlorobenzene (ng/Nm^3)	4 321	3 161	3 968	4 884•
Cadmium (mg/Nm^3)	0.9	0.8	0.8	0.6
Lead (mg/Nm^3)	13.5	15.2	15.2	8.4
Chromium (mg/Nm^3)	0.04	0.03	0.1	0.03
Nickel (mg/Nm^3)	0.2	0.3	0.5	0.5
Mercury (mg/Nm^3)	0.7	0.5	0.9	0.5
Antimony (mg/Nm^3)	0.6	2.6	0.5	0.5

Table XVI continued:

	Stack Emissions per tonne of Feed (as fired)			
TSP (g/tonne)	843	874	977	682
HCl (g/tonne)	4 400	4 130	4 480	3 930
PCDD (µg/tonne)	428	400	228	516
PCDF (µg/tonne)	570	574	340	411
PCB (µg/tonne)	3 413	245	ND	574*
PAH (µg/tonne)	29 305	33 201	26 956	54 514*
Chlorophenol (µg/tonne)	18 403	15 042	10 814	28 973*
Chlorobenzene (µg/tonne)	18 014	12 807	16 061	22 045*
Cadmium (g/tonne)	3.8	3.0	3.2	2.6
Lead (g/tonne)	54.8	57.8	60.0	34.2
Chromium (g/tonne)	0.2	0.1	0.4	0.1
Nickel (g/tonne)	1.0	1.0	2.2	1.9
Mercury (g/tonne)	2.8	2.0	3.6	2.2
Antimony (g/tonne)	2.3	9.6	2.1	1.9

* based on average of two tests only
ND - Not Detected

The distributions of PCDD and PCDF homologue congener groups in the stack emissions for the four test conditions are illustrated in Figures 8 and 9. The amount of PCDD homologue was found to increase with increasing degree of chlorination for all four conditions. The distribution of the PCDF homologues took on a bell-shaped form centered about the hexa-CDFs. The homologue distributions for the PCDDs and PCDFs do not vary significantly between the various test conditions.

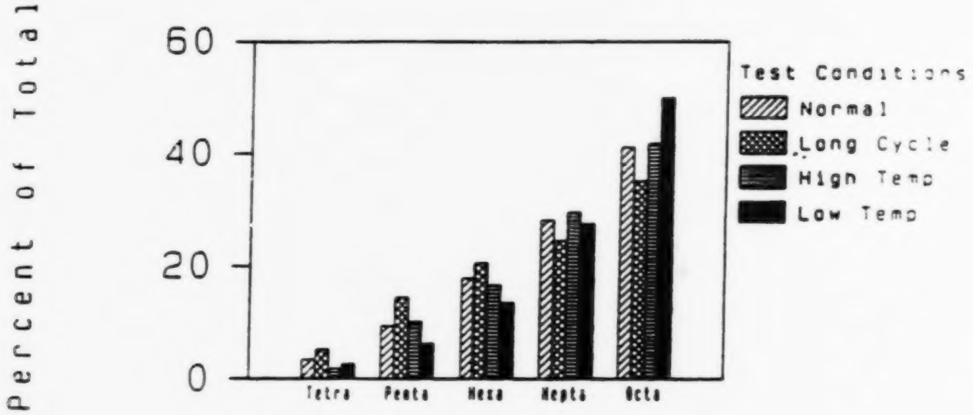


Figure 8: Stack Dioxin Homologue Distribution by Test Condition (P.E.I. Incinerator)

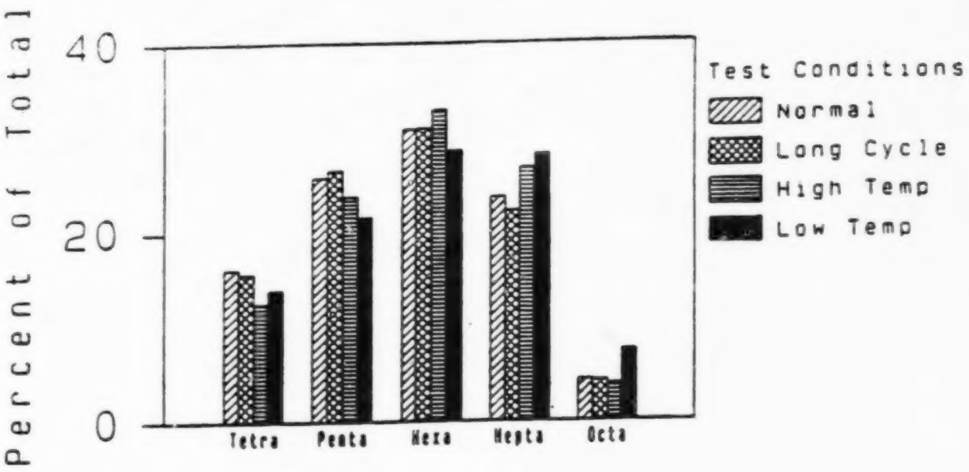


Figure 9: Stack Furan Homologue Distribution by Test Condition (P.E.I. Incinerator)

The concentrations of the various organic compound classes were compared at the boiler inlet and at the stack (see Table XVII). The PCDD and PCDF concentrations measured at the boiler inlet were low or not detected for all three conditions differing from the normal. The concentrations at the stack were in all cases higher than at the boiler inlet.

The PCB concentrations were higher at the stack except for the high temperature condition, however this result is doubtful since PCBs were only detected for one run at the boiler inlet and at very near the detection limit. Chlorophenol concentrations were significantly higher at the stack whereas the concentrations of PAH were found to be higher at the boiler inlet. Group averages for the chlorobenzene concentrations were misleading since a wide variation of levels were found between individual runs.

The possibility of chemical transformations occurring upon cooling of the flue gas was suggested as an explanation for the higher levels of some compounds in the stack as compared to the boiler inlet.

Table XVII: Concentrations of Organic Compounds at Boiler Inlet in Comparison to Stack

	Concentration (ng/Nm^3 @ 12% CO$_2$)					
	Long Cycle		High Temperature		Low Temperature	
Compound	Boiler Inlet	Stack	Boiler Inlet	Stack	Boiler Inlet	Stack
PCDD	ND	107	1	62	14	123
PCDF	ND	156	ND	95	10	98
PCB	11*	58	8*	ND	61	126**
PAH	10 475	8 010	12 226	6 653	29 481	12 490**
Chlorophenol	486	3 773	479	2 706	2 941	6 591**
Chlorobenzene	6 595	3 161	4 895	3 968	8 906	4 884**

* only one non-zero value (two readings were below detection limit)
** based on average of 2 tests only.

The mass flow rates of PCDDs and PCDFs entering with the refuse and the mass flow rates of the stack emissions are compared in Figure 10. These results show that although the amounts of PCDDs and PCDFs in the input garbage are quite different, the emissions for all four test conditions are very similar. In fact these results imply that the operating parameters do not have a significant effect on the levels of the PCDDs and PCDFs emitted.

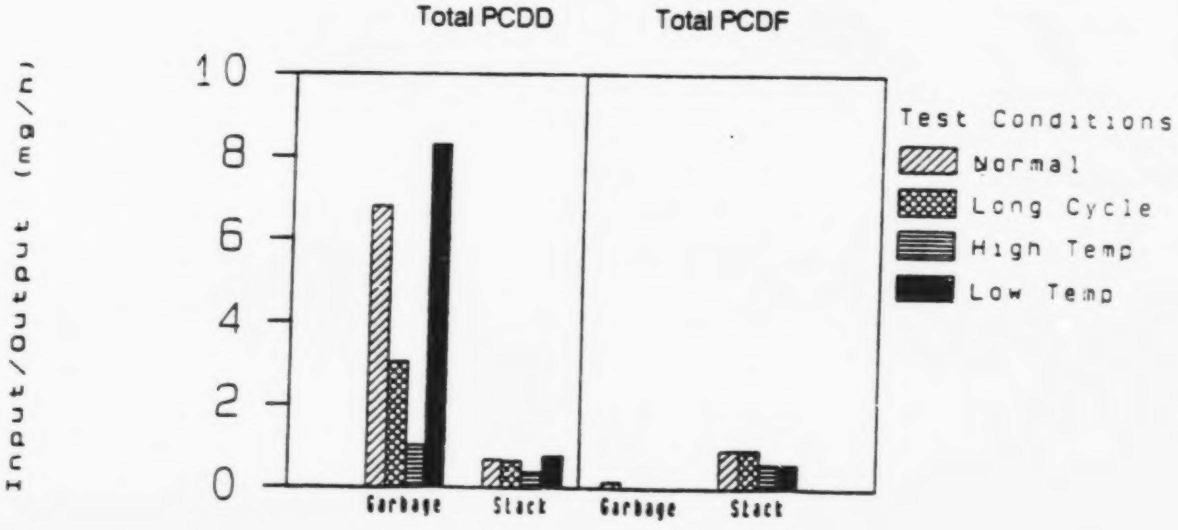


Figure 10: Total Dioxin/Furan Input/Output

The concentrations of PCDDs and PCDFs in the incoming refuse and the ashes collected from three different sites within the incinerator were also compared. Figure 11 illustrates the differences in the incoming levels with the levels found in the different ashes (averaged for 12 test runs, i.e. triplicate runs of the four test conditions). No dioxins or furans were detected in the bottom ash samples. The PCDDs were approximately equally distributed between the boiler and economizer ashes while the PCDF distribution appears to be slightly biased towards the economizer ash (however, the variation between the runs is not reported and therefore this difference may not be significant).

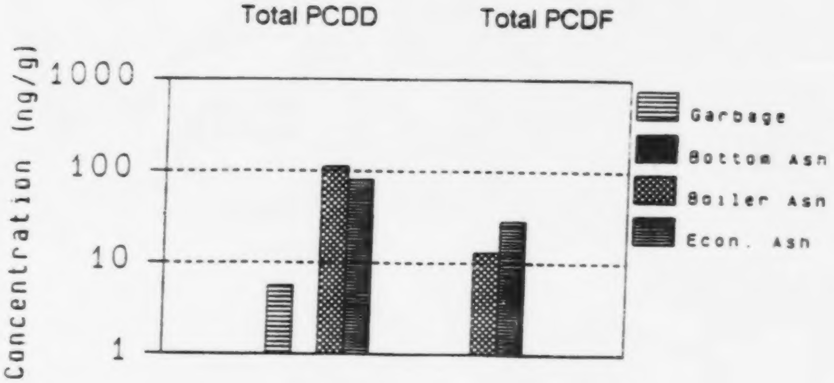


Figure 11: Distribution of Dioxins/Furans in Solids (as analysed)

The significance of these results is misleading if one does not consider the relative amounts of each ash. The incinerator bottom ash comprises about 98.5% of the total ash, boiler ash about 1.25%, and economizer ash makes up about 0.13% of the total. In addition, one must also consider the reduction of refuse to fly ash on a weight-to-weight basis.

The distribution of chlorophenols (CP), PCBs, PAHs, and chlorobenzenes (CB) analyzed for in the garbage and the collected ashes are shown in Figure 12.

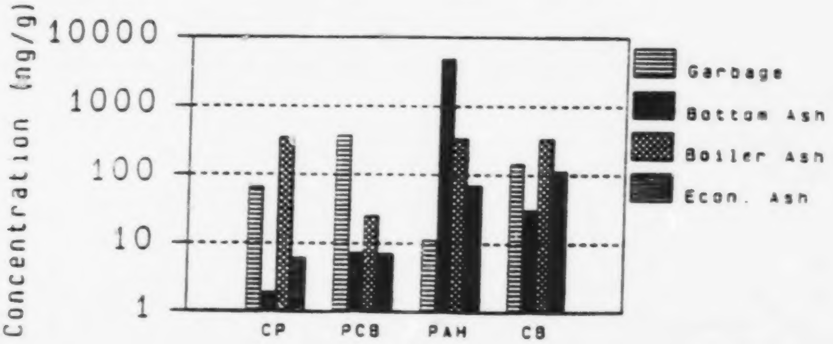


Figure 12: Distribution of Organics in Solids (as analysed)

The range of operating conditions for which the two-stage incinerator was tested do not reveal any significant differences with respect to the PCDD/PCDF emission levels. The system efficiently removes PCDDs and PCDFs from the stack emissions regardless of the which particular set of operating conditions were used. Good design of flue gas scrubbing systems and controlled operation of the incinerator appear to minimize the emissions of concern.

Most of the modern municipal waste incinerators tend to be operated under much more careful control than their older counterparts. Increasingly stringent regulations and technological improvements in the design of flue gas cleaning systems have resulted in lower emissions in the modern incinerator. NITEP undertook this study (EPS Canada, 1986) because the role of emission control technology was not fully evaluated by conducting full-scale or large-scale pilot tests, previously.

Extensive testing was performed on two pilot-scale air pollution control systems:

1. Wet-dry scrubber (sprayer-dryer) plus fabric filter
2. Dry scrubber plus fabric filter

These designs were tested for the efficiencies in reducing the emission of organic compounds, including PCDDs and PCDFs, as well as heavy metals and acid gases such as hydrogen chloride and sulphur dioxide. The emissions of these contaminants were studied as function of the operating conditions in order to determine optimal conditions for incinerator operation. The study involved the determination of the compounds of concern in the emissions and the ashes resulting from the incineration process.

The incinerator on which the pilot plant studies were carried out was a mass burning design. The refuse was burned as received in a water-wall furnace and steam was produced from the flue gas heating of the recovery boilers. The incinerator plant consisted of four incinerators, each rated at 227 tons per day, which were connected to a common ash storage pit and stack. A cross-sectional diagram of one incinerator is shown in Figure 13. Each incinerator consists of a vibrating feeder-hopper, feed chute, drying/burning/burn out grates, refractory-lined burning zone, a waste heat recovery boiler with super heater and economizer, a two-field electrostatic precipitator, an induced draft fan, and a wet ash quench/removal system.

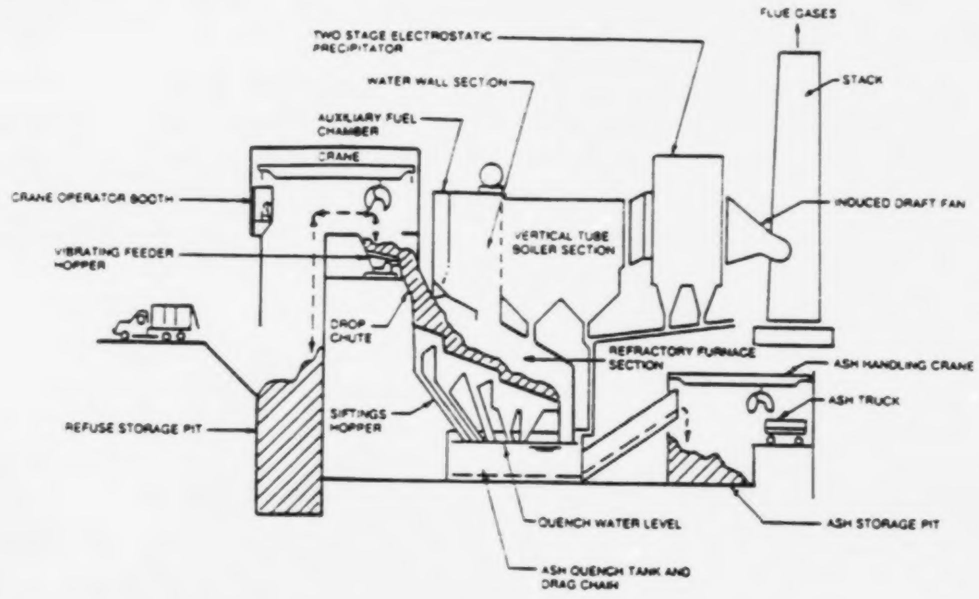


Figure 13: Quebec Incinerator Schematic Cross-Section

The system was modified for the pilot-scale studies by installing a flue gas take-off duct at the inlet to one of the electrostatic precipitators, as shown in Figure 14. The study was set up to evaluate the performance of the pilot plant in both the dry and wet-dry modes of operation.

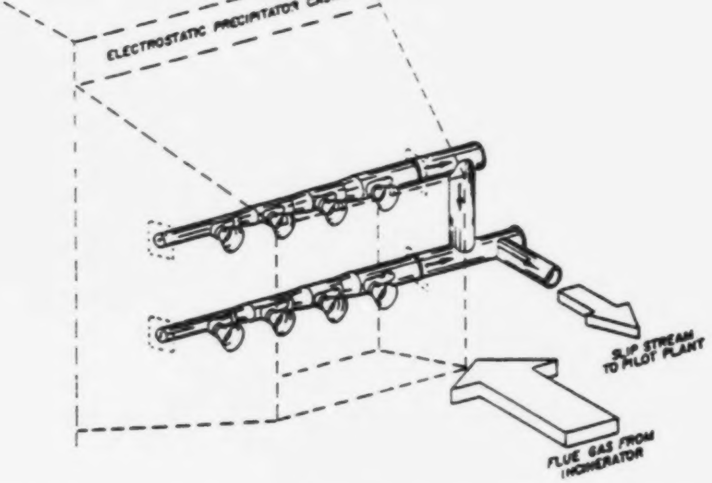

ELECTROSTATIC PRECIPITATOR CASING
SLIP STREAM TO PILOT PLANT
FLUE GAS FROM INCINERATOR

Figure 14: Incinerator Gas Slip Stream Take-off Arrangement

The dry system, as shown in Figure 15, consists of a single dry lime injection nozzle and an internal cyclone. The hot flue gas first enters the wet-dry scrubber which in this mode of operation is used only to cool the gas. The flue gas enters this chamber at a temperature of 255-270 °C and is cooled to 110-140 °C by a water spray. The cooled flue gas enters the bottom of the dry scrubber tangentially with respect to the internal cyclone where large particles of fly ash are removed. A dry, hydrated lime powder is injected in a stream of compressed down upon the gas stream. The chemical treatment of the flue gas results in a dry stream of particles and lime which continues on towards the fabric filter dust collector. The fabric filter is a single compartment baghouse containing a 6 x 12 array of 72 high-temperature Teflon bags with Gortex scrim (air-to-cloth ratio of 4.4). The bags are cleaned using low pressure air pulses directed downward from discharge nozzles located above the bags. The two major advantages of dry scrubbing versus wet scrubbing are the absence of a liquid effluent and the reduced corrosion of equipment.

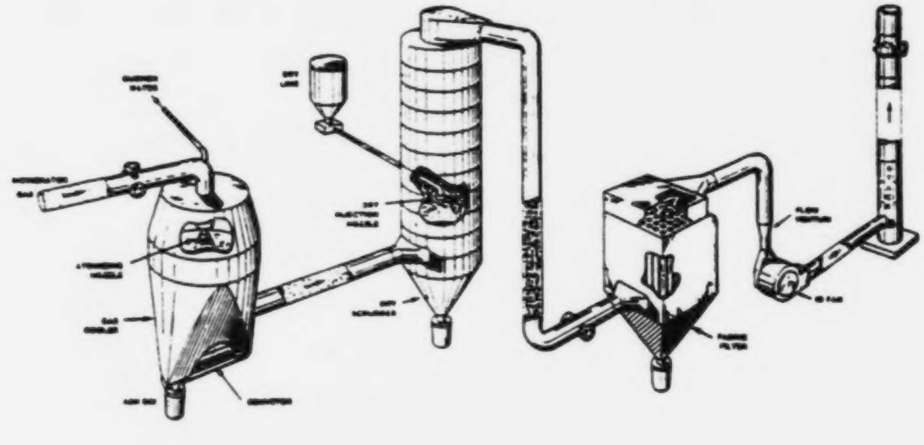


Figure 15: FLAKT's Dry-System

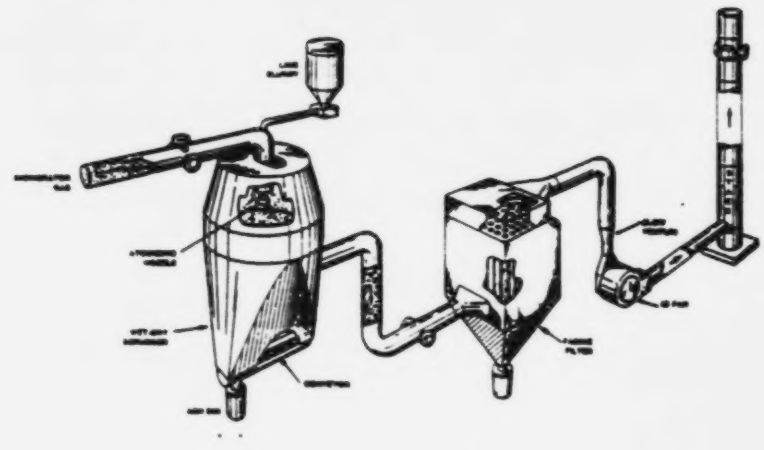


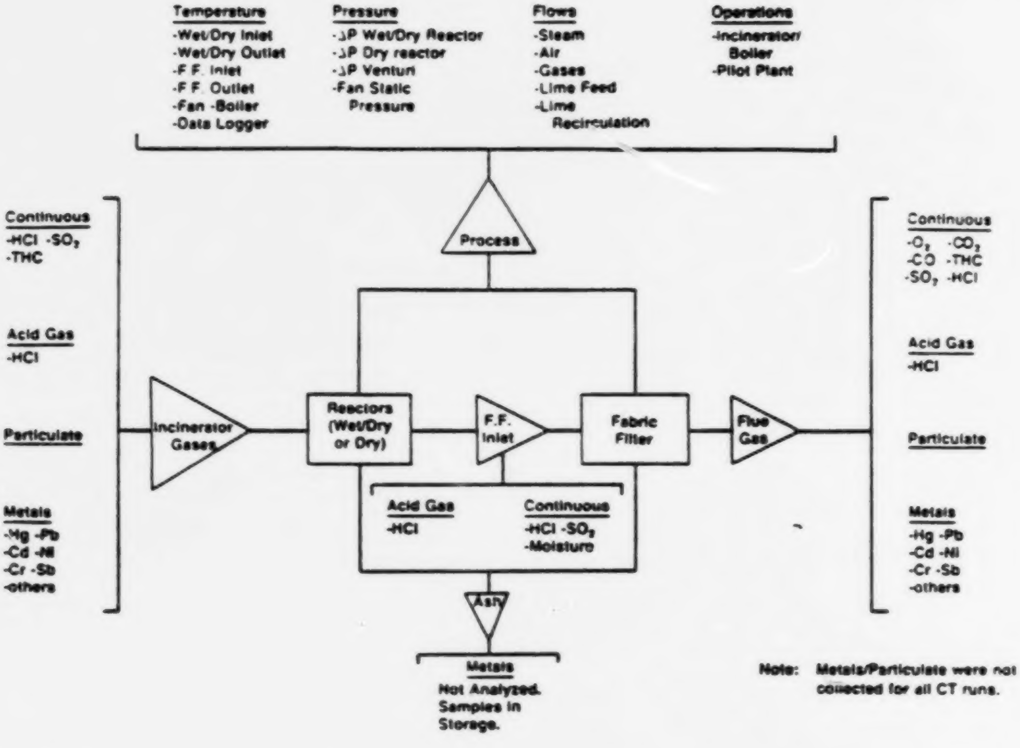
Figure 16: FLAKT's Wet-dry System

Reproduced from
best available copy.

In the wet-dry mode of operation, the scrubber receives hot flue gas from the top of the vessel, as shown in Figure 16. The flue gas is thoroughly mixed with a spray of finely atomized lime slurry. The slurry is carefully mixed in proportion to the flue gas so that all the water is evaporated, leaving the lime as suspended fine particulates in the gas. The wet-dry scrubber creates a cool, dry mixture of particles (110-140 °C) similar to that produced in the dry scrubbing process. The entrained particulates are passed on towards the fabric filter system previously described.

Both the dry and wet-dry systems can be operated with recycling of the fabric filter ash by mixing the ash, which contains some unreacted lime, with fresh lime in either the dry or slurried form.

As was done for the previous NITEP study on the two-stage incinerator, characterization tests were done an a wide variety of operating conditions to determine the parameters to be used for the intensive performance evaluation. The parameters measured during the characterization testing phase are outlined in Figure 17. Both scrubber systems were tested over a range of operating temperatures and hydrated lime feed rates since these were the two most important independent variables. The characterization test conditions studied are summarized in Table XVIII.



Note: Metals/Particulate were not collected for all CT runs.

Figure 17: Parameters Measured during Characterization Testing

Reproduced from best available copy

Table XVIII: Summary of Characterization Test Conditions

	Temperature After Cooling			
Operating Mode	Target °C	Actual °C	Lime Feed Rate	Test No.
Dry System				
Normal Temp. Operation	140	145	Normal	11
	140	151	High	4
	140	152	High (+ Recycle)	5
	140	151	Very high	3
High Temp. Operation	>200	222	Very high	2
Low Temp. Operation	125	133	Normal (+ Recycle)	12
Wet-Dry System				
Normal Temp. Operation	150	156	Normal	6, 10
	150	158	High	8
	150	158	High (+ Recycle)	9
	150	156	Very high	7
Low Temp. Operation	135	141	Normal	13
	135	144	Normal (+ Recycle)	14

Six performance test conditions were selected as outlined in Table XIX. A wide range of scrubber temperatures (i.e. temperature of the flue gas leaving the scrubber) were chosen in order to investigate the influence of this variable on the removal of acid gases, mercury, and organic compounds. The lime feed rate was maintained at normal levels as established by the characterization tests to permit closer study of the effect of temperature on the removal efficiencies. The fabric filter temperature was kept between 110 to 140 °C for all test runs in order to evaluate the scrubber temperature dependence. This temperature can be controlled by adjusting the slurry addition rate in the wet-dry system or the rate of water spray in the case of the dry system. The flow of flue gases through the system was controlled to ensure constant flows were used during the tests. The performance test conditions are summarized in Table XX and some of the key operating parameters are listed in Table XXI.

Table XIX: Selection of Performance Test Conditions

Operating Mode	Target Temp. Before Fabric Filter (°C)	Rationale
Dry System	>200	To collect data with no gas cooling for comparison to the three other temperatures.
	140	Benchmark for comparison with other tests. Considered normal for full-scale.
	125	To observe potential improvements in organic removal at lower than normal temperatures.
	110	To push the limits of low temperature operation, particularly for impact on organics removal.
Wet-Dry System	140	Benchmark for comparison with other tests.
(+ Recycle)	140	To investigate whether lime recycle enhances the removal efficiency of organics and acid gases.

Table XX: Summary of Performance Test Conditions

	Temperature before Fabric Filter	
	Target °C	Actual °C*
Dry System	> 200	209
	140	141
	125	125
	110	113
Wet-Dry System	140	140
(+ Recycle)	140	141

* Thermocouple Data from Pilot Plant Control System

Table XXI: Summary of Key Operating Parameters

	Dry System				Wet-Dry System	
	110°C	125°C	140°C	>200°C	140°C	140°C "Recycle"
INCINERATOR						
- Steam Flow (kg/h x 10^3)	32.8	33.4	33.2	33.0	32.1	31.3
- Gas Temp.-Boiler Outlet (°C)	303	287	291	287	278	293
FABRIC FILTER						
- Pressure Drop (cm water gauge)	15.7	14.4	14.9	14.7	15.2	15.9
LIME						
- Flow (kg/h)	3.7	3.6	3.7	3.6	3.5	3.5
TEMPERATURE (°C)*						
- Inlet to Pilot Plant	267	258	261	253	254	263
- Inlet to Fabric Filter	113	125	142	209	140	141

* Thermocouple data from pilot plant control system.

Sampling and data collection were done for duplicate runs of each test condition. Incinerator operations were found to be quite stable throughout the test program and pair averages were therefore used to represent the results of each test condition. Although in general pair group averages were concluded to provide a relative indication of the levels of emission, seemingly significant differences were sometimes seen in results between a pair of runs for the same condition.

To evaluate the performance of the two pollution control systems, the emissions were sampled at:

1. The pilot plant inlet (i.e. between the incinerator and pilot plant) to characterize the untreated raw gas coming from the incinerator

2. The midpoint between the scrubber system and the fabric filter to evaluate the scrubber performance

3. The stack to evaluate the performance of the pollution control system as a whole.

The ashes collected in the hoppers (ash bins) of the scrubber and fabric filter vessels were also subjected to analysis. The results for the emissions of PCDDs, PCDFs, and other chlorinated organics are discussed in the ensuing sections. Before treating the results, it is necessary to mention the detection limits for the analytical methodology employed in this study (entries of "ND" in the tables implies that the levels were below the detection limit). For the analysis of PCDDs and PCDFs in flue gas samples, the limits of detection per analyte peak were:

- 0.2 ng for Cl_4DD, Cl_4DF, Cl_5DF, Cl_6DF
- 0.4 ng for Cl_5DD, Cl_6DD, Cl_7DF, Cl_8DF
- 0.6 ng for Cl_7DD, Cl_8DD

The concentrations of PCDDs and PCDFs in the flue at the three sampling locations for each test condition are given in Tables XXII and XXIII. The same results are given in Figure 18 in order to more readily illustrate the efficiency of the scrubbers and fabric filter in removing PCDDs and PCDFs. The removal efficiencies were calculated and are given in Tables XXII and XXIII. The overall removal of PCDDs was greater than 99.9% for all tests except for the high temperature condition where the efficiency was slightly lower (99.4%). The stack emissions all had very low PCDD contents (all below 6 ng/Nm^3) and were not even detectable for most of the test runs. The overall removal efficiencies for PCDFs ranged from 99.3 to greater than 99.9%. Clearly, both systems under all test conditions are very efficient in removing PCDDs and PCDFs from the flue gas.

Drawing conclusions regarding the removal efficiencies for the different scrubbers under the conditions studied should perhaps be avoided since the most important consideration should be the overall performance of the air pollution control equipment. In Table XXIII, one can see that for the wet-dry system at both operating conditions the efficiency for PCDF removal at the midpoint (i.e. for the wet-dry scrubber) is negative. This implies the formation of PCDFs somewhere after the inlet to the pilot plant. The overall efficiencies of these two operating conditions, however, were amongst the highest observed for the entire test program. Therefore the only significant conclusion to be drawn from these results is that there does not appear to be any advantage (with respect to emission of PCDDs and PCDFs) to using one scrubbing design or set of operating conditions over the other as long as a fabric filter is used following the scrubber.

Table XXII: PCDD Concentrations [ng/Nm^3 @ 8% O$_2$] in Flue Gas and Efficiency of Removal

	Dry System				Wet-Dry System	
	110°C	125°C	140°C*	200°C	140°C	140°C + Recycle
Inlet [ng/Nm^3]	580	1,400	1,300	1,030	1,100	1,300
Midpoint [ng/Nm^3]	310	570	540	1,140	840	1270
Outlet [ng/Nm^3]	0.2	N.D.	N.D.	6.1	N.D.	0.4
Efficiency [%]						
- Inlet/Midpoint	47	60	57	- 11	24	2
- Overall	>99.9	>99.9	>99.9	99.4	>99.9	>99.9

* based on one test

Table XXIII: PCDF Concentrations [ng/Nm^3 @ 8% O$_2$] in Flue Gas and Efficiency of Removal

	Dry System				Wet-Dry System	
	110°C	125°C	140°C*	200°C	140°C	140°C + Recycle
Inlet [ng/Nm^3]	300	940	1,000	560	660	850
Midpoint [ng/Nm^3]	270	440	630	490	690	1,030
Outlet [ng/Nm^3]	2.3	N.D.	N.D.	6.1	N.D.	0.9
Efficiency [%]						
- Inlet/Midpoint	11	54	37	13	- 4	- 21
- Overall	99.3	>99.9	99.9	99.8	>99.9	99.9

* based on one test

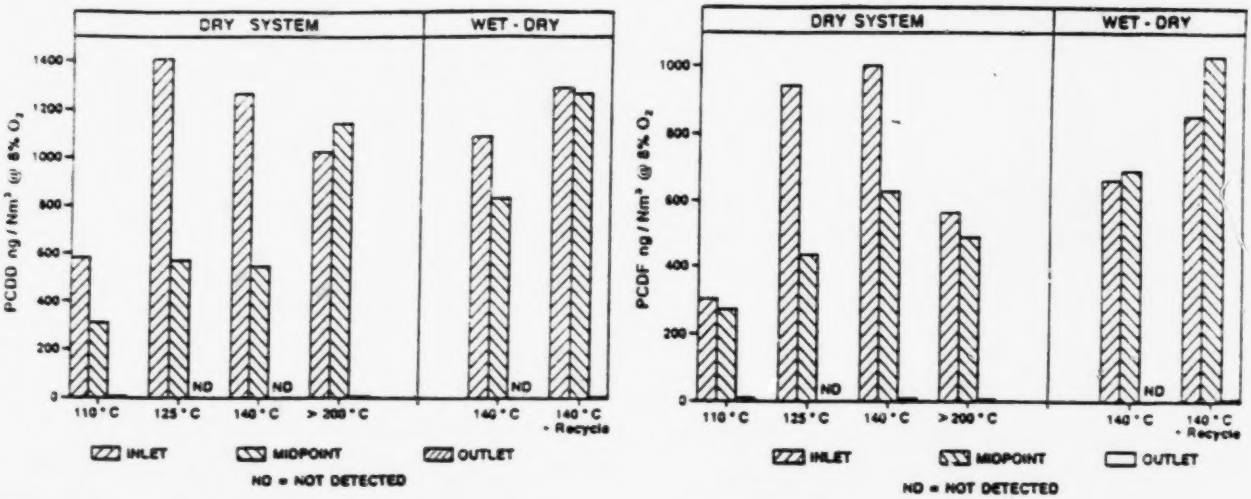


Figure 18: PCDD (left) and PCDF (right) Concentrations in Flue Gas

It is interesting to note that the distribution for PCDD homologues takes on a crude bell-shape centered about the hepta-CDDs while the concentration of PCDF homologues appears to decrease within increasing degree of chlorination. These distribution patterns are somewhat different than those reported by other workers.

The overall removal efficiencies for other chlorinated organic compounds are given in Table XXIV. Only the high-temperature dry scrubber/fabric filter combination shows a generally poor efficiency in removing organic material. The best system appears to be the wet-dry system operated with a continuously fresh feed of lime slurry.

In addition to sampling the flue gas at different points in the incinerator system, hopper ashes were collected in each vessel of the pilot plant. As the flue gas moves throughout the system, some of the fly ash falls out and is collected in the scrubbers while the remainder is largely collected by the fabric filter. The approximate proportion of the ash collected in each vessel is given in Table XXV. The concentrations (ng/g) of PCDDs in the various ashes for the different test conditions are listed in Tables XXVI and XXVII and illustrated in Figure 19. The proportion of PCDDs found in each hopper does not match the proportion of fly ash distributed amongst the hoppers. Presumably the distribution of fly ash particles of different sizes is also not proportional to the relative amounts of the ash collected in each hopper. One would expect the smaller particles to travel further along the system. No mention was made regarding the distribution of ash particles nor was any correlation made between particle sizes and the level of PCDDs present. The highest concentration of PCDDs were found in the fabric filter ash for all of the test conditions studied. The ash in this vessel should consist largely of the smaller particles. The resulting surface area would be very high (for a given weight of ash, the smaller the particle, the larger the total surface area) and thus more PCDDs would be expected to be present due to the greater degree of adsorption per unit weight of fly ash. The same sort of trends are apparent for the concentrations of PCDFs found in the various ashes collected (see Table XXVI and Figure 19). The highest concentrations of PCDFs were found in the fabric filter ashes for all six conditions.

Table XXIV: Percent Removal of Other Organics

	Dry System				Wet-Dry System	
	110°C	125°C *	140°C	200°C	140°C	140°C + Recycle
Chlorobenzenes	95	98	98	62	>99	99
PCB	72	>99	>99	54	>99	>99
PAH	84	82	84	98	>99	79
Chlorophenols	97	99	99	56	99	96

* based on one test

Table XXV: Proportion of Ash Collected in Each Vessel
(Note: Excludes incinerator bottom ash and boiler ash)

Source of Ash	Dry System	Wet-Dry System
Wet-Dry Scrubber (or Conditioning Tower)	30 %	33 %
Dry Scrubber	40 %	----
Fabric Filter	30 %	67 %
	100 %	100 %

Table XXVI: PCDD Concentrations in Ash [ng/g]

	Dry System				Wet-Dry System	
Operating Condition	110°C	125°C	140°C	200°C	140°C	140°C + Recycle
Wet-Dry Scrubber Ash	13	14	6	6	6	12
Dry Scrubber Ash	160	64	94	31	N/A	N/A
Fabric Filter Ash	280	570	570	740	160	230

N/A Not Applicable

Table XXVII: PCDF Concentrations in Ash [ng/g]

	Dry System				Wet-Dry System	
Operating Condition	110°C	125°C	140°C	200°C	140°C	140°C + Recycle
Wet-Dry Scrubber Ash	10	12	4	5	5	82
Dry Scrubber Ash	87	36	68	22	N/A	N/A
Fabric Filter Ash	160	320	380	320	130	170

N/A Not Applicable

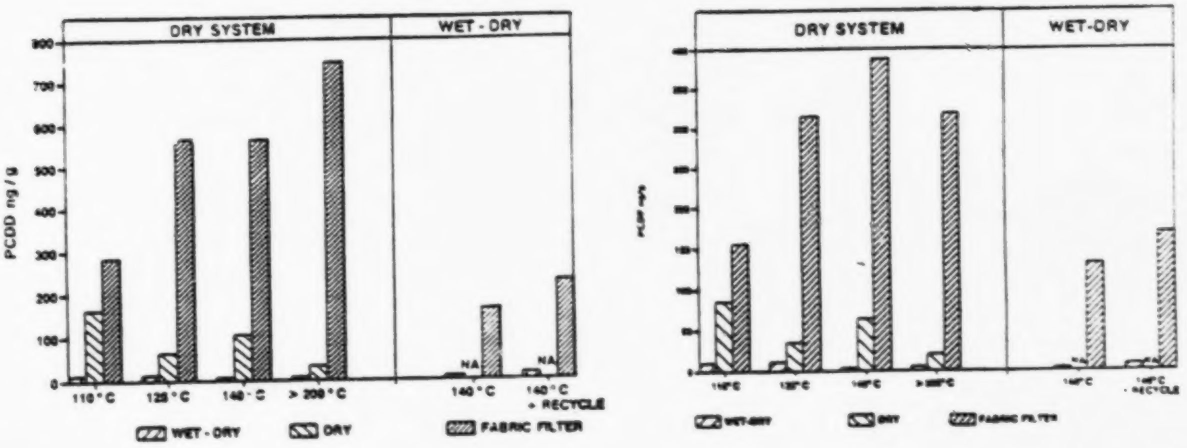


Figure 19: PCDD (left) and PCDF (right) Concentrations [ng/g] in Hopper Ashes

The distribution of the PCDD and PCDF homologues in the hopper ashes are shown in Figures 20 and 21, respectively. The homologue distributions of the PCDDs and the PCDFs in the fabric filter ash are very similar to their corresponding homologue distributions for the inlet flue gas. This should not be too surprising considering that the bulk of the dioxins and furans are trapped at the fabric filter. In fact, for the dry scrubber system, approximately 80% of the PCDDs and 75% of the PCDFs are found in the fabric filter ash. For the wet-dry system, about 98% of the PCDDs and 98% of the PCDFs are present in the fabric filter ash. The PCDD and PCDF concentrations in the other hopper ashes are too low to permit any reasonable conclusions from being drawn.

The concentrations of organic compounds, other than PCDDs and PCDFs, are shown in Figure 20. The highest concentrations, as for the PCDDs and PCDFs, were found in the fabric filter flyash. This also implies that the larger surface area per unit weight of ash will result in higher concentrations per gram of ash for the smaller particles, which would be expected to collect mainly in the fabric filter.

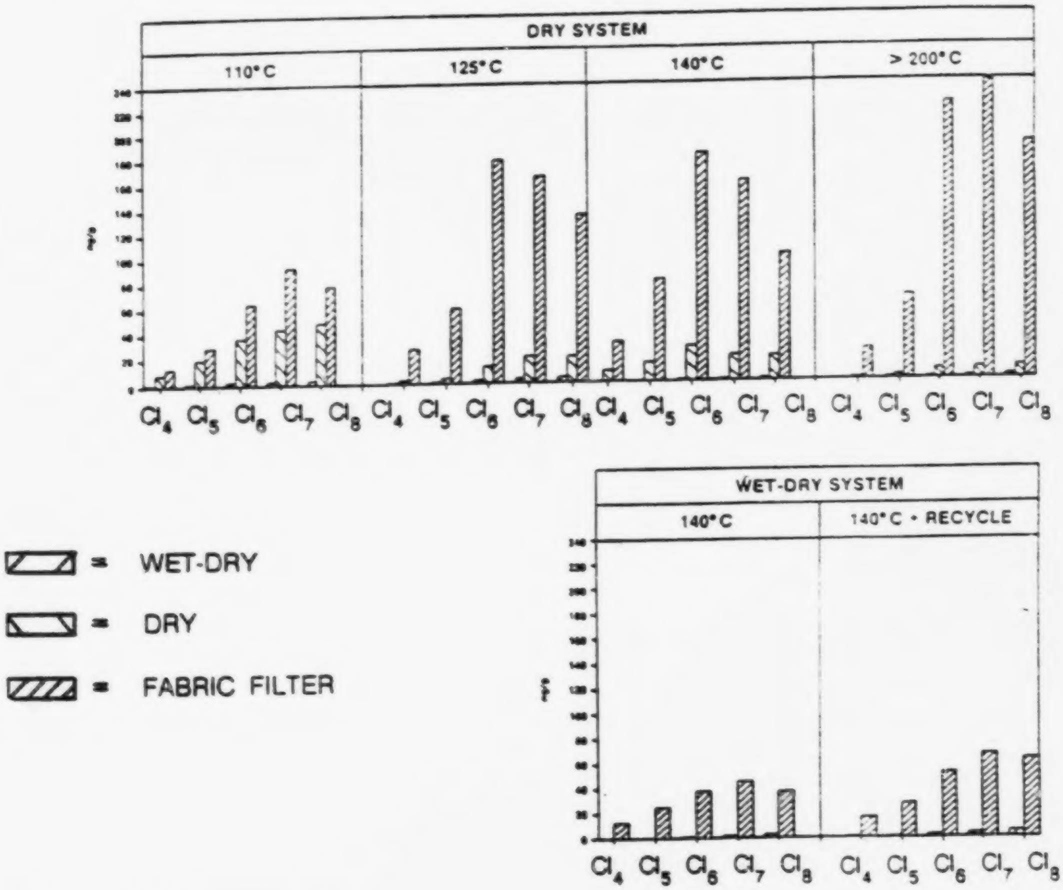


Figure 20: PCDD Homologue Distribution in Hopper Ashes [ng/g]

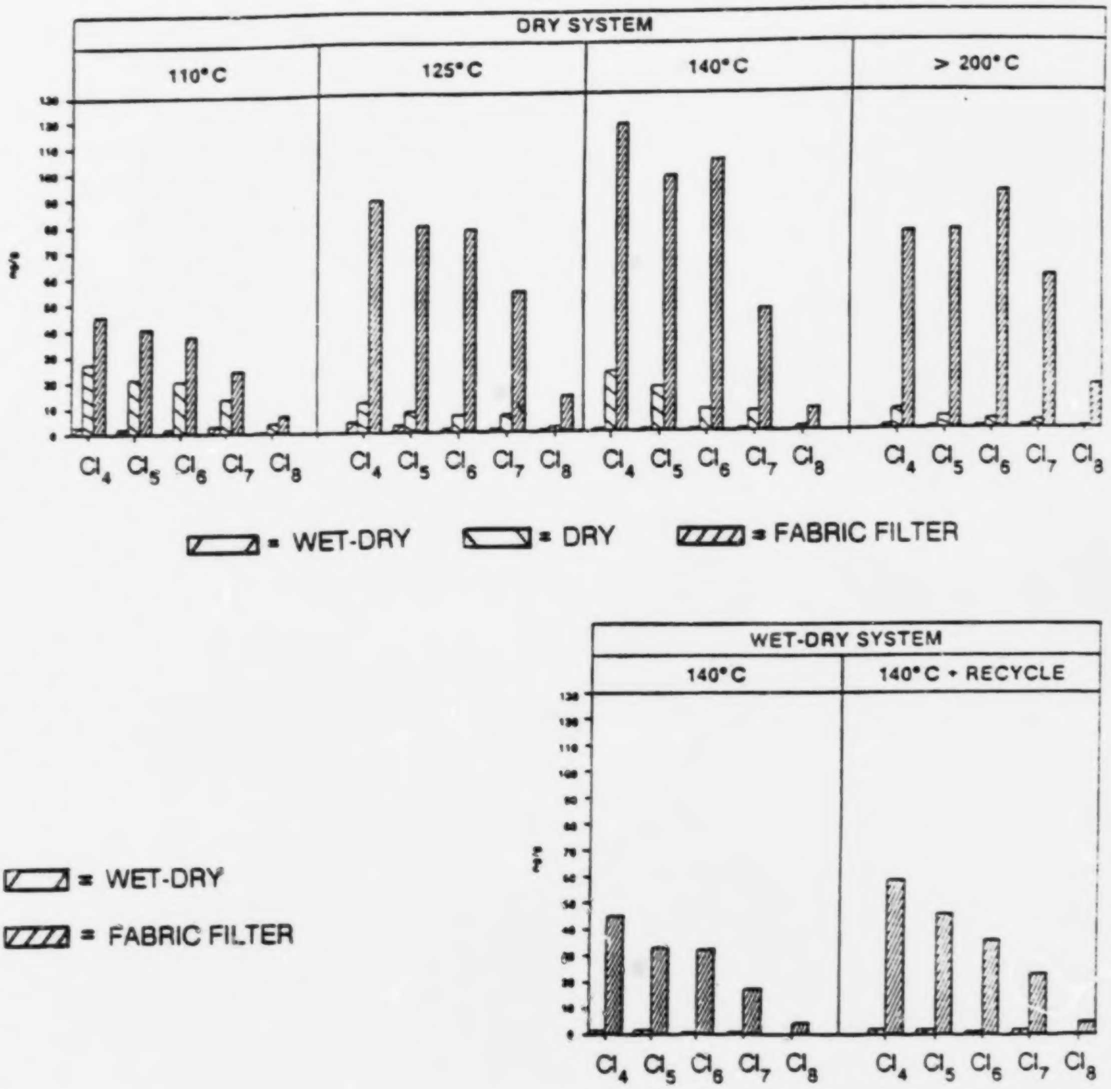


Figure 21: PCDF Homologue Distribution in Hopper Ashes [ng/g]

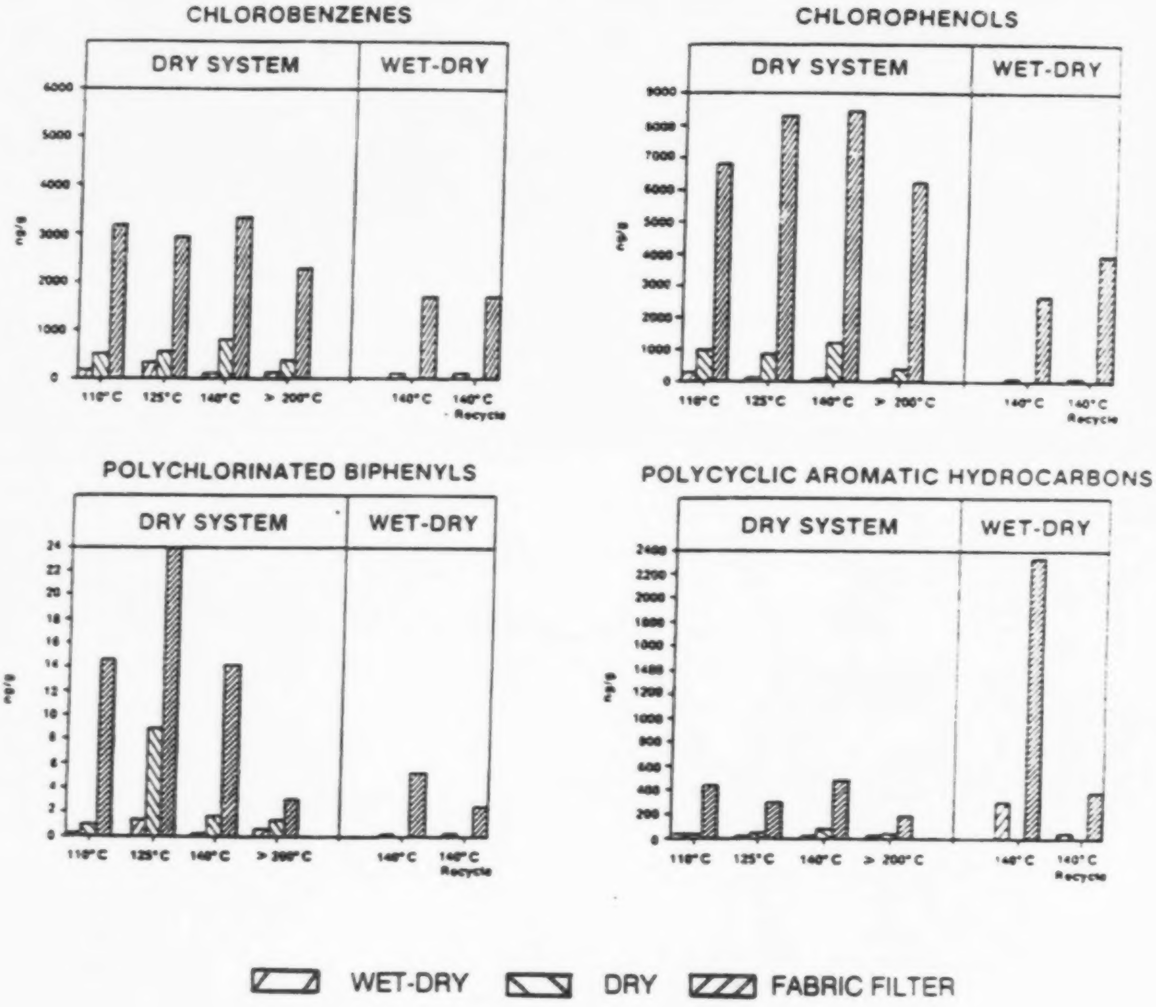


Figure 22: Concentrations of Chlorobenzenes, Chlorophenols, Polychlorinated Biphenyls, and Polycyclic Aromatic Hydrocarbons in Hopper Ashes

Reproduced from best available copy.

The conclusions of this study are:

1. Both dry and wet-dry systems, when used in conjunction with a fabric filter, were very effective for removing pollutants. Neither system showed a significant difference in removal efficiency.

2. Cooling of the flue gas temperature below 200 °C was a key parameter in both systems for the removal of hydrogen chloride, sulphur dioxide, and mercury.

3. Removal efficiencies for PCDD and PCDF were very high (>99% for all tests) and for most runs, the concentrations of PCDDs and PCDFs emitted after the air pollution control system approached the detection limits of the analytical methodology used in the study.

4. Highest concentrations of PCDDs and PCDFs were found in the fabric filter ash (expected since the fabric filter exhibited high removal efficiency for PCDDs and PCDFs).

5. Other trace organic compounds were efficiently removed (80-99%) by both scrubber/fabric filter systems operated under cooled flue gas conditions.

6. Concentrations of the other trace organic compounds in the various hopper ashes followed a similar pattern as observed for PCDDs and PCDFs.

7. Heavy metal collection efficiencies generally exceeded 99.9% for both systems, except for mercury for which high removal was obtained only for cooled flue gas conditions.

3.2 Municipal Waste Incinerator Studies Canada, Sweden, and Germany

In a study similar to that carried out under Canada's NITEP, a pilot plant consisting of a spray dryer adsorption chamber and baghouse was set up to study its effectiveness in removing PCDDs and PCDFs from municipal waste incinerator flue gas (Nielsen et al., 1986). The pilot plant is illustrated in Figure 23 and its operating parameters are given in Table XXVII. This system was tested on a municipal incinerator which received household and light industrial waste. The incinerator had a capacity of about 10 tons/hour, a temperature of 850-900 °C, a flue gas rate of 50,000 Nm^3/h, and an outlet oxygen concentration of 10.5-11.5%. The flue gas, introduced through a gas disperser at the top of the scrubber vessel, and the hydrated lime slurry, introduced via a spray atomizer, are intimately mixed. The flue gas was sampled at two sites, before and after the scrubber/baghouse combination, SDA_{in} and BH_{out}, respectively. The sampling apparatus used in the measurements is shown in Figure 24. The heated area is kept at a temperature equal to that of the gas in the duct at the sampling point to minimize adsorption or desorption of organic vapours on the particulates. The results obtained for two test runs are given in Tables XXVIII and XXIX. The only difference between the two runs was the temperature of the gas at the outlet of the spray dryer absorption chamber. The outlet temperature in the first run was considerably higher than in the second run. It should be noted that the temperature at the SDA in sampling site (280-300 °C) is high enough to permit the formation of PCDDs as it has been illustrated (Dickson, 1987). The inlet concentrations may not be realistic, however this is not critical since the main concern is the level of PCDDs and PCDFs emitted at the stack. Higher levels of PCDDs and PCDFs were observed for the test condition with the higher gas SDA outlet temperature. While it is difficult to make conclusions based on this work since only one run at each condition was reported and the reproducibility has not been demonstrated, the temperature of the gas exiting the scrubber was claimed to be as significant variable as in the NITEP study (EPS Canada, 1986).

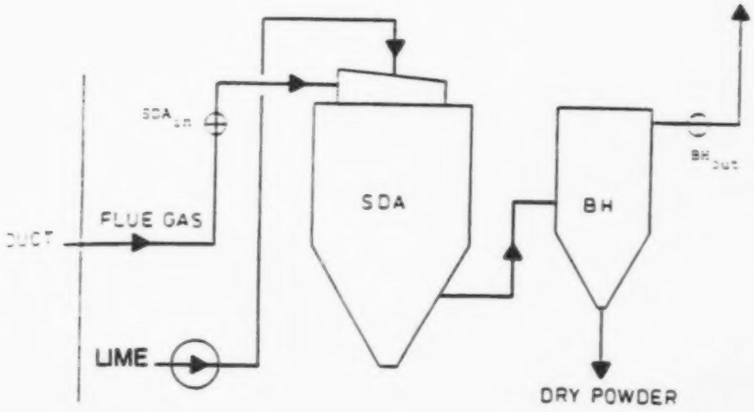


Figure 23: Municipal Waste Incinerator (Pilot Plant) with Spray Absorption by Rotary Atomizer

Table XXVII: Average Parameters and Conditions of the Flue Gas Cleaning System

		SDA$_{in}$	BH$_{out}$
Gas Temp.	°C	280-300	100-160
HCl	mg/Nm^3	400-500	4
SO$_2$	mg/Nm^3	60-130	5
Particulate	mg/Nm^3	2,000	10
Gas Flow	Nm^3/h	300	

1	Stack
2	Glass probe
3	Heated oven
4	Glass cyclone
5	Quarts fiber thimble
6	Cooler
7	Condensate collector
8	XAD-2 adsorber
9	Heater
10	To pump and volume meter

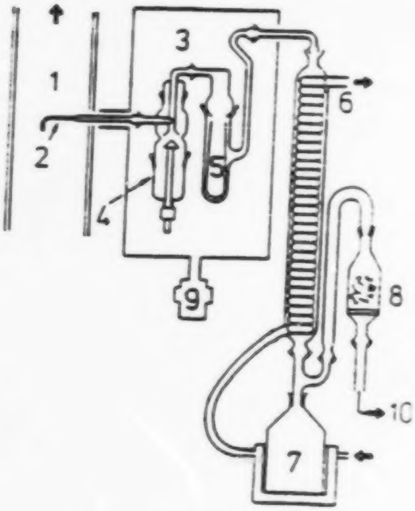


Figure 24: Flue Gas Sampling System (by Studsvik Energiteknik, Sweden)

Table XXVIII: Gasphase PCDD and PCDF Removal, Run 1 (Inlet Samples)

Compound	SDA_{in} [ng/Nm^3]	BH_{out} [ng/Nm^3]	Removal [%]
2,3,7,8 Cl_4DD	0.13	<0.04	
1,2,3,7,8 Cl_5DD	3.5	0.4	
ΣCl_4DD	2.1	<1.0	>52
ΣCl_5DD	52	13	75
ΣCl_6DD	67	4.9	93
ΣCl_7DD	25	4.4	82
Cl_8DD	Not analyzed	Not analyzed	
Σ PCDD	146	23	84
2,3,7,8 Cl_4DF	1.0	0.3	
1,2,3,7,8 Cl_5DF	10	0.9	
2,3,4,7,8 Cl_5DF	8.5	0.8	
ΣCl_4DF	37	0.9	98
ΣCl_5DF	97	12	88
ΣCl_6DF	48	6.8	36
ΣCl_7DF	55	4.3	92
Cl_8DF	Not analyzed	Not analyzed	
Σ PCDF	237	24	90

Table XXIX: Gasphase PCDD and PCDF Removal, Run 2 (Inlet Samples)

Compound	SDA_{in} [ng/Nm^3]	BH_{out} [ng/Nm^3]	Removal [%]
2,3,7,8 Cl_4DD	1.7	<0.02	
1,2,3,7,8 Cl_5DD	4.2	<0.02	
ΣCl_4DD	12.7	0.35	>97
ΣCl_5DD	46	<0.2	>99.6
ΣCl_6DD	38	<0.2	>99.5
ΣCl_7DD	50	<0.2	>99.6
Cl_8DD	88	<0.2	>99.8
Σ PCDD	235	<1.15	>99.5
2,3,7,8 Cl_4DF	3.1	<0.02	
1,2,3,7,8 Cl_5DF	13	<0.02	
2,3,4,7,8 Cl_5DF	3.8	<0.02	
ΣCl_4DF	61	<0.35	99.4
ΣCl_5DF	99	<0.35	99.6
ΣCl_6DF	122	<0.30	99.7
ΣCl_7DF	115	<0.20	>99.8
ΣCl_8DF	134	<0.20	>99.8
Σ PCDF	531	<1.4	>99.7

In another study refuse burned at two Canadian incinerators was investigated. The average composition of this refuse is given in Table XXX (Tosine et al., 1985). The levels of PCDDs and PCDFs found in representative samples for each incinerator are listed in Table XXXI. In all cases the levels of PCDDs were higher than those for PCDFs. In fact, PCDFs were only found in one sample of refuse. Similar findings were later reported by NITEP (EPS Canada, 1986). For the PCDDs, the higher chlorinated species, in particular Cl_8DD and Cl_7DDs, were the dominant isomers.

Table XXX: Average Composition of Refuse in Two Ontario Incinerators [%]

Paper and Textile	56
Garden and Foodstuff	16
Metal and Glass	15
Plastic and Rubber	13

Table XXXI: Concentrations of PCDD and PCDF in Refuse Samples from Two Ontario Incinerators.
Concentrations given in [ng/g]

	Incinerator A			Incinerator B		
Test	1	2	3	1	2	3
Cl_4DD	ND*	ND*	ND*	1.5	ND*	ND*
Cl_5DD	ND	ND	ND	2.7	ND	ND
Cl_6DD	ND	ND	ND	26	22	ND
Cl_7DD	2.0	5.3	19	28	87	20
Cl_8DD	8.0	6.5	11	36	330	55
Total	10	12	30	94	440	75
Cl_4DF	ND	ND	ND	0.8	ND	ND
Cl_5DF	ND	ND	ND	41	ND	ND
Cl_6DF	ND	ND	ND	7.7	ND	ND
Cl_7DF	ND	ND	ND	9.0	ND	ND
Cl_8DF	ND	ND	ND	0.8	ND	ND
Total	ND	ND	ND	22	ND	ND

* None detected at the isomer detection limits ranging from 1 pg/g for tetrachlorinated to 4 pg/g for octachlorinated species.

All data corrected for recovery of internal spike (Cl^{37} Cl_8DD).

In addition to determining the PCDD and PCDF contents of the refuse, the levels of PCBs, chlorophenols, and chlorobenzenes present in the incoming waste were studied. The results for these chlorinated compounds are given in Table XXXII. It should be noted that these values were given for the total amounts of the higher chlorinated isomers, those containing more than 2 chlorine atoms. The analytical methodology employed in this study was not suitable for the lower chlorinated isomers and therefore the levels in Table XXXIII represent the minimum amounts present in the garbage.

Table XXXII: Concentrations of Chlorinated Organics in Refuse Samples from Two Ontario Incinerators
Concentrations in [ng/g]

	Incinerator A			Incinerator B		
Test	1	2	3	1	2	3
PCB	110	1,500	200	120	120	110
Chlorobenzenes	34	41	45	10	10	5
Chlorophenols	150	240	680	420	600	570

This study illustrates that levels of PCDDs and PCDFs in the refuse feedstock should be considered in studies dealing with mass balances in the incineration process. The presence of potential precursors such as PCBs and the chlorinated phenols and benzenes in the initial refuse may also play a significant role in the amounts of PCDDs and PCDFs formed during the incineration of municipal refuse.

In the fall of 1984 and the spring of 1985, 15 experiments were carried out at the municipal solid waste incinerator located in Umea, Sweden (Rappe et al., 1986). The experiments carried out are summarized in Table XXXIII along with the corresponding results of the PCDD and PCDF levels given in terms of ng of "TCDD equivalents" per Nm^3 of dry gas (10% CO_2). The total levels of PCDDs and PCDFs as expressed in terms of ng equivalents of Cl_4DD were found to vary relatively little over the ten day period in which the experiments were conducted. The actual levels of the individual PCDD and PCDF homologues were not included in the report and thus it is difficult to get a full comprehension of this data without this information. Although it is important to get some understanding regarding the significance of results in terms of toxicity, analytical information must not be sacrificed. In future studies, results should be not be given only in terms of "TCDD equivalents".

Table XXXIII: Experiments at the Municipal Waste Incinerator in Umea, Sweden

Experiments	No of exp	Temp °C		ng TCDD equivalent in Nm^3
		mean	range	
Normal conditions (fall)	3	803	736-846	9
Normal with wood chips	2	764	737-790	10
Normal with oil burner	2	827	811-842	11
Low temperature	3	539	484-580	11
Low with oil burner	3	625	602-658	10
Start-up	1	-	20-790	54
Start-up with oil burner	1	-	28-816	12
Normal conditions (spring)	3	784	700-850	5.6

Table XXXIV lists a comparison of results for a study of several incineration and related processes, again given in terms of "TCDD equivalents". In the laboratory pyrolysis of PVC (SARAN), a series of PCDFs were produced while only very low amounts of PCDDs were found. Based on this result, PVC may potentially act as a precursor for the formation of PCDDs and PCDFs in incinerators. When one compares the chromatographic profiles of penta-CDFs produced from municipal incineration, PVC pyrolysis, and hexachloroethane pyrolysis, the patterns are quite similar despite the fact that the chlorine contents of the burn materials were 1%, 57%, and 90%, respectively.

Table XXXIV: Comparison of Emissions from Incineration and Related Processes in Sweden

Place	Type	Mean Value "TCDD equivalents" [ng/Nm^3] d g 10% CO_2
Umea, fall	MSW cross-gate	10
Umea, spring	MSW cross-gate	5.6
Avesta, fall	MSW cross-gate	80
Avesta, spring	MSW cross-gate	2.0
Boras	MSW cross-gate	38
Mid Sweden	MSX fluid-bed	1.8
Rönnskär	Ind. copper melter	11
Mid Sweden	Ind. steel melter	0.8 ng/g
Laboratory	SARAN pyrolysis	0.15 ng/g

In one study, fly ash samples from six different municipal incinerators from four different countries were compared (Tong and Karasek, 1986). Very similar isomer distributions for PCDDs and PCDFs were found between incinerators even though the concentration of the dioxins and furans in the ashes varied considerably. This finding implies that the PCDDs and PCDFs were formed through the same mechanisms, independent of the garbage composition or incinerator design. Although different incinerator designs and operating conditions have been studied and their refuse characterized, the information reported in the literature is quite scattered. Therefore the mechanism for the formation of PCDDs and PCDFs in incinerators still has not been conclusively proven.

Figure 25 shows the isomeric distribution patterns for the Cl_4DDs, Cl_4DFs, Cl_5DDs, and the Cl_5DFs for four of the fly ash samples studied. The distributions are very similar within a given congener group for all the fly ashes. This trend is also observed for the other congener groups.

Table XXXV gives the concentrations of the tetra-, penta-, and hexachlorinated dioxins and furans for all of the samples analyzed. The Machida incinerator fly ash had the lowest levels of PCDDs and PCDFs. This incinerator first segregated its refuse into classes and then burned only the combustible material. Metal waste and plastics were not fed into the incinerator. The remaining incinerators studied did not sort their refuse prior to burning.

Table XXXV: Quantitative Comparison of Some Selected PCDD/PCDF in Fly Ash from Different Countries

	Ontario	Oslo	Paris	Kyoto	Hiroshima	Machida
Cl_4DD	436	27	18	8	29	0.2
Cl_5DD	504	77	50	17	95	0.8
Cl_6DD	668	149	142	38	149	4
Cl_4DF	294	55	81	15	90	2
Cl_5DF	508	74	136	23	92	7
Cl_6DF	420	80	192	22	85	12

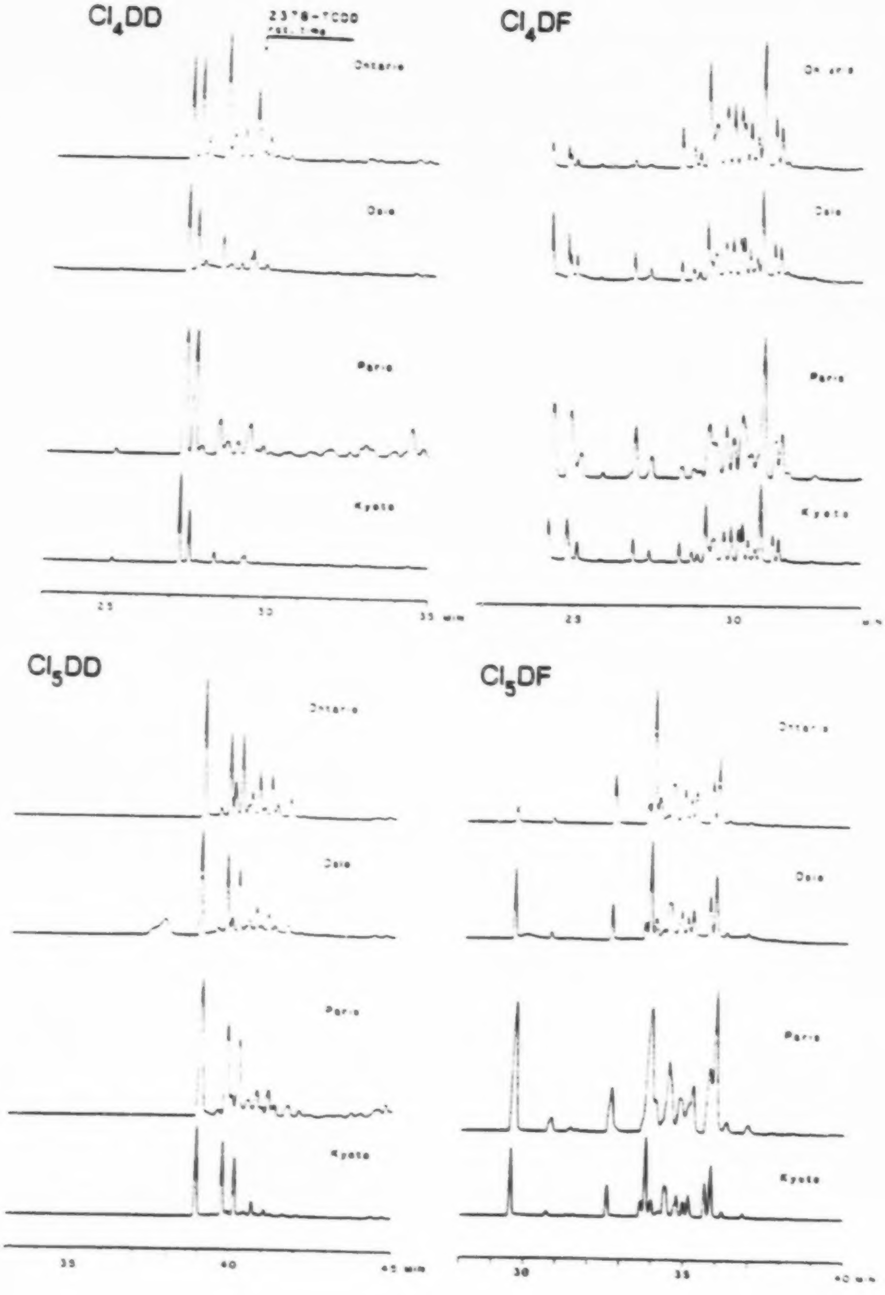


Figure 25: GC/MS/SIM Data Showing the Isomer Distribution Pattern of Some Selected PCDD and PCDF in the Fly Asn Samples Collected from Different Countries

Reproduced from best available copy

A comparison of PCDD and PCDF concentrations in the flue gases of five different municipal waste incinerators located in Germany and representing normal operating conditions are given in Table XXXVI (Nottrodt and Ballschmiter, 1986). From this information, typical ranges of PCDD and PCDF contents in the flue gases of municipal incinerators were defined as shown in Table XXXVII. It must be noted that these stack gas concentrations are actually the sum of the PCDDs/PCDFs found in the particulate and gaseous phase. The particulate content of the stack gases ranged from 10-20 mg/m^3.

Table XXXVI: PCDD/PCDF-Contents in Flue Gases from Municipal Waste Combustors

Date	2,3,7,8 Cl_4DD	Σ Cl_4DD	Cl_8DD	2,3,7,8 Cl_4DF	Σ Cl_4DF	Cl_8DF
14.-19.12.81	0.16	4	49		22	8
09.04.84	0.2	24	14	3.0	64	5
11.04.84	0.2	25	11	3.0	66	1
01.05.84	0.7	19	15	2.0	110	2
02.05.84	0.6	19	14	6.0	144	2
04.05.84	0.05 ±0.09	5	5	0.9	38	1
15.05.84	0.1	7	13	1.4	41	4
17.05.84	0.1	6	16	1.4	31	1.4
27.03.85	0.2	2.6	5	1.4	40	1.2
29.03.85	0.5	5.1	13	2.9	59	3.4
30.03.85	0.4	5.1	15	2.5	53	3.7
01.04.85	0.3	3.3	15	1.5	34	7.8
02.04.85	0.1	2.1	4	1.2	29	1.5
03.04.85	0.2	3.5	9	2.1	48	2.8

Table XXVII: Typical Ranges of PCDD/PCDF-Contents in Flue Gases and Residues from Municipal Waste Combustors

Flue Gas:	2,3,7,8-Cl_4DD	0.05 - 0.07	ng/m^3
	Σ Cl_4DD	4 - 25	ng/m^3
	Σ Cl_5DD (3-7)	20 - 145	ng/m^3
	Cl_8DD	4 4 - 9	ng/m^3
	2,3,7,8-Cl_4DF	0.9 - 6	ng/m^3
	Σ Cl_4DF	22 - 144	ng/m^3
	Σ Cl_5DF (3-7)	91.361	ng/m^3
	Cl_8DF	1 - 8	ng/m^3
Clean Gas Dust:		0.25 - 3	ng/g
Filter Dust:		1.2 - 1.4	ng/g
Blag:		< 20	pg/g

A mass burning municipal incinerator was operated under two different load conditions and the levels of PCDDs and PCDFs produced under these conditions were studied (Nottrodt and Ballschmiter, 1986). The purpose of this study was to investigate the influence of the time at which the flue gas flowing through the combustion chamber was held above 800 °C. Regular operating parameters are given in Table XXXVIII along with the parameters used during the sampling done for this study. Two 24 hour runs were used for each of the two different load conditions.

At a charging rate of 16 Mg/h, the amount of steam produced is 52.4 Mg/h. The studied load conditions were chosen as those required to produce about 45 and 30 Mg/h steam. Thus the residence time at greater than 800 °C for the flue gas under load condition 1 should be approximately two-thirds that of load condition 2.

Table XXXVIII: Normal Operating Parameters of the Plant

Charging Rate	16	mg/h
At Max. Heating Value	11,100	kJ/kg
Grid Area	60	m^2
Steam Production	52.4	mg/h
Steam Temperature	400	°C
Steam Pressure	40	bar
Gas Cleaning	1. Electrost. Precipitator 2. Wet Scrubber	

Parameters During Sampling

	Steam	Temperature		Flue Gas,Wet
		1	2	
	[g/h]	[°C]	[°C]	[ml/h]
Load 1	45	1,090	950	100,000
Load 2	30	1,050	880	70,000

Temperature 1	Combustion Chamber
Temperature 2	Top of Boiler

The PCDD and PCDF contents of the fly ash and filter dust (combined prior to sample preparation and analysis) for the duplicate tests of the load conditions are given in Tables XXXIX and XL. Each run was characterized by the 24 hour averages of steam production and the temperatures in the combustion chamber and at the top of the boiler. The incinerator was operated at constant conditions during the 24 hour runs. The standard deviations of one hour averages for steam production and temperature were within 1-2% of the 24 hour averages. The PCDD and PCDF levels under both conditions are quite low. The levels under load 2 generally appear to be lower than the levels under load 1, however this may not be statistically significant. The variation in the levels between the duplicate runs for the same load is sometimes quite large in comparison with the average of the two runs. Therefore care must be taken in making any conclusions.

Table XXXIX: PCDD-Contents in Fly Ash and Filter Dust

Load	Steam Mg/h	Temperature 1 [°C]	Temperature 2 [°C]	ΣCl_4DD ppb	183 ppb	189 ppb	201 ppb	202 ppb	205 ppb	210 ppb
1	44.9	1,088	947	1.4	0.87	0.3	0.6	1.7	0.9	80
1	44.6	1,088	950	1.2	0.1	0.5	1.2	3.9	2.1	215
2	31.0	1,052	878	1.6	0.1	0.4	0.7	1.8	1.2	81
2	31.7	1,049	882	0.9	0.1	0.4	0.7	1.6	1.0	42

Table XL: PCDF-Contents in Fly Ash and Filter Dust

Load	Steam Mg/h	Temperature 1 [°C]	Temperature 2 [°C]	ΣCl_4DF ppb	83 ppb	117 ppb	121 ppb	135 ppb
1	44.9	1,088	947	14.8	0.6	1.1	1.0	10
1	44.6	1,088	950	9.7	0.4	1.0	1.1	18
2	31.0	1,052	878	8.1	0.3	0.8	0.6	10
2	31.7	1,049	882	9.5	0.4	0.8	0.6	11

83	2,3,7,8 Cl_4DF	189	1,2,3,7,8 Cl_5DD
117	2,3,4,7,8 Cl_5DF	201	1,2,3,4,7,8 Cl_6DD
121	1,2,3,6,7,8 Cl_6DF	202	1,2,3,6,7,8 Cl_6DD
135	Cl_8DF	205	1,2,3,7,8,9 Cl_6DD
183	2,3,7,8 Cl_4DD	210	Cl_8DD

Temperature 1	Combustion Chamber
Temperature 2	Top of Boiler

The concentrations of PCDDs and PCDFs in the stack flue gas were also determined and are given in Tables XLI and XLII. The concentrations are again quite low and load 2 appears to have slightly lower levels than for load 1. Limitations inherent with the sampling of flue gases and variations between duplicate runs do not permit any conclusive statements.

Table XLI: PCDD-Contents, Flue Gas

Load	Steam mg/h	Temperature 1 [°C]	Temperature 2 [°C]	Σ Cl_4DD ng/m^3	183 ng/m^3	189 ng/m^3	201 ng/m^3	202 ng/m^3	205 ng/m^3	210 ng/m^3
1	44.9	1,088	947	5.1	0.5	0.9	0.8	1.6	1.0	13
1	44.6	1,088	950	5.1	0.4	0.6	0.6	1.7	0.9	15
2	31.8	1,052	878	3.3	0.3	0.7	0.6	1.1	0.8	15
2	31.7	1,049	882	2.1	0.1	0.3	0.3	0.7	0.5	4

Table XLII: PCDF-Contents, Flue Gas

Load	Steam mg/h	Temperature 1 [°C]	Temperature 2 [°C]	Σ Cl_4DF ng/m^3	83 ng/m^3	117 ng/m^3	121 ng/m^3	135 ng/m^3
1	44.9	1,088	947	59	2.9	4.7	4.1	3.4
1	44.6	1,088	950	53	2.4	4.1	5.6	3.7
2	31.8	1,052	878	34	1.5	2.0	1.0	7.8
2	31.7	1,049	882	29	1.2	2.6	3.0	1.5

83	2,3,7,8 Cl_4DF	189	1,2,3,7,8 Cl_5DD
117	2,3,4,7,8 Cl_5DF	201	1,2,3,4,7,8 Cl_6DD
121	1,2,3,6,7,8 Cl_6DF	202	1,2,3,6,7,8 Cl_6DD
135	Cl_8DF	205	1,2,3,7,8,9 Cl_6DD
183	2,3,7,8 Cl_4DD	210	Cl_8DD

A study on the formation of PCDDs and PCDFs in a refuse-derived fuel (RDF) fired incinerator compared the levels formed when the boilers were operated under RDF-natural gas firing and RDF-only firing (see Tables XLIII and XLIV) (Hahn et al., 1986). The levels of PCDDs and PCDFs produced were low for all for all tests performed but were typical of the levels reported in studies conducted on other incinerators. The inconsistencies observed in the operation of the incinerator do not permit any conclusions being made regarding the correlation of operating conditions with the resulting levels of PCDDs and PCDFs emitted.

Table XLIII: Comparison of PCDD and PCDF Emissions during RDF-Only and RDF-Natural Gas Firing

Test Series	Homologue Group	Average ng/Nm^3 PCDD at 12% CO_2	Average ng/Nm^3 PCDF at 12% CO_2	PCDD/PCDF Ratio
RDF-Natural Gas at 9.4% CO_2				
	Cl_4	23	56	
	Cl_5	232	55	
	Cl_6	232	13	
	Cl_7	191	3	
	Cl_8	23	3	
	Total	701	130	5.39:1
RDF-Only at 10% CO_2				
	Cl_4	19	43	
	Cl_5	125	28	
	Cl_6	68	5	
	Cl_7	91	1	
	Cl_8	13	2	
	Total	316	79	4.00:1

Table XLIV: Comparison of 2,3,7,8-Cl_4DD, 2,3,7,8-Cl_4DF, and Cl_4DF Emissions during RDF-Only and RDF-Natural Gas Firing

	CO_2	2,3,7,8-Cl_4DD	ΣCl_4DD	2,3,7,8-Cl_4DD of Total Cl_4DD	2,3,7,8-Cl_4DF	ΣCl_4DF	2,3,7,8-Cl_4DF of Total Cl_4DF
	[%]	[ng/Nm^3 at 12% CO_2]			[ng/Nm^3 at 12% CO_2]		
RDF-Natural Gas	9.4	0.34	27.9	1.22	2.45	44.8	5.47
	9.3	0.50	18.6	2.69	2.43	48.5	4.99
	9.5	0.70	22.1	3.17	4.04	74.3	5.44
Average	9.4	0.51	22.9	2.36	2.97	55.9	5.30
RDF-Only	10.1	0.81	20.2	4.01	2.88	41.8	6.89
	9.9	0.40	12.9	3.10	2.17	36.2	5.99
	10.0	0.52	24.2	2.15	3.00	51.2	5.86
Average	10.0	0.58	19.1	3.09	2.68	43.1	6.25

The emissions of two Belgian incinerators under routine operations were studied over a one year period by taking samples daily for two weeks in each of the four seasons (De Fré, 1986). The average concentrations of PCDDs and PCDFs in the total gas stream for each incinerator are summarized in Table XLV. The waste burned at incinerator I is fairly homogeneous and is representative of average Belgian municipal refuse, with the addition of some waste from small industries. Incinerator II is located in a rural community. The refuse presented to it is poor in caloric value and is often made up with city waste from a different source. Neither incinerator was equipped with an energy recovery system and therefore gases are emitted at relatively high temperatures.

The standard deviations calculated for the results given in Table XLV are of the same magnitude and usually larger than the averages themselves. These averages were obtained from values which often consisted of a large number of low measurements plus fewer high measurements that tend to contribute more to the value of the average. For example, two Cl_5DD isomers (or possibly artifacts) were present at extremely high concentrations (10.3 $\mu g/Nm^3$) on one day at incinerator I; if this measurement was omitted, the results in the parentheses would be obtained.

The emission factors, the number of mg of PCDD/PCDF produced per ton of refuse, are given in Table XLV. It was not possible to obtain statistically significant conclusions from the small differences observed because of the irregular distribution and large standard deviations for the data collected. The furnace temperatures were operated in a range from 800 to 1,050 °C and no clear relationship to the levels of PCDDs and PCDFs emitted was found. By observation of incinerator II, waste could be classified into two distinct sources, urban and rural refuse. For the days on which only urban waste was burned, the average sum of the dioxin and furan concentrations was nearly twice that observed when only rural refuse was incinerated. The urban waste was found to produce higher furnace temperatures and yield higher chlorine content in the flue gases. Since the PVC content was not measured directly (it was estimated from the HCl concentrations in the gases based on the assumption that PVC is the most important source of organic chlorine and the fact that PVC gives a nearly 100% yield of HCl on combustion), no relationship between the amount of PVC and the emission of PCDDs and PCDFs could be determined.

Table XLV: Average Emission Concentration in [ng/Nm^3] (left side) and Emission Factors [mg/ton] (right side)

Average Emission Concentration in [ng/Nm^3]			Emission Factors [mg/ton]	
Component	Incinerator I	Incinerator II	Incinerator I	Incinerator II
PCDD (4-8) total	1,005	354	13.3	3.1
Cl_4DD	20	40	0.27	0.35
2,3,7,8-Cl_4DD	0.97	3.8	0.015	0.038
Cl_5DD	396	34	5.2	0.3
Cl_6DD	185	53	2.5	0.46
Cl_7DD	206	67	2.7	0.59
Cl_8DD	202	153	2.68	1.34
PCDF (4-8) total	1,185	1,216	15	6.9
Cl_4DF	116	196	1.5	1.0
2,3,7,8-Cl_4DF	9	36	0.14	0.22
Cl_5DF	209	188	2.7	0.97
Cl_6DF	318	372	4.3	1.9
Cl_8DF	204	433	2.6	1.5

3.3 Municipal Waste Incineration in Japan

Approximately 110,000 tons of municipal refuse are produced daily in Japan of which about 68% is incinerated (as of 1983) (Hiraoka et al., 1986). The incinerators are operated in three different modes:

1. Fully continuous (24 hour operation)
2. Semi-continuous (16 hour operation)
3. Batch incineration (8 hour operation).

The presence of dioxins in the fly ash from a Japanese incinerator was first reported in 1979 (Eiceman et al., 1979). In 1984 an extensive survey of 33 municipal waste incinerators was conducted in which the flue gas, fly ash, bottom ash, and waste water were analyzed for their PCDD and PCDF contents. The results of this study are summarized below.

Fly Ash (35 samples):

- Cl_4DDs ranged from ND to 14.5 ng/g; averaged 1.6 ng/g
- Cl_5DDs ranged from 2.7 to 10,700 ng/g; averaged 523 ng/g
- Cl_5DFs ranged from 1.0 to 1,510 ng/g; averaged 150 ng/g
- 2,3,7,8-Cl_4DD ranged from ND to 4.7 ng/g (12 samples analysed)

ND = < 0.05 ng/g

Bottom Ash (30 samples):

- Cl_4DDs ranged from 0.3 to 7.3 ng/g; averaged 1.6 ng/g
- Cl_5DDs ranged from 5.0 to 2470 ng/g; averaged 216 ng/g
- Cl_5DFs ranged from 2.3 to 864 ng/g; averaged 81.9 ng/g
- 2,3,7,8-Cl_4DD ND (11 samples analyzed)

ND = < 0.05 ng/g

Flue Gas (25 samples):

- Cl_4DDs ranged from ND to 109 ng/Nm^3; averaged 54.9 ng/Nm^3
- Cl_5DDs ranged from 133 to 13,600 ng/Nm^3; averaged 1,510 ng/Nm^3
- Cl_5DFs ranged from 436 to 10,000 ng/Nm^3; averaged 2,520 ng/Nm^3
- 2,3,7,8-Cl_4DD ND (1 sample analyzed)

ND = < 2 ng/Nm^3

Discharged Waste Water (17 samples):

- Cl_4DDs ranged from ND to 9.7 ng/L; 12 samples were ND
- Cl_5DDs ranged from ND to 46.7 ng/L; 8 samples were ND
- Cl_5DFs ranged from ND to 285 ng/L; 8 samples were ND

ND not defined for water samples

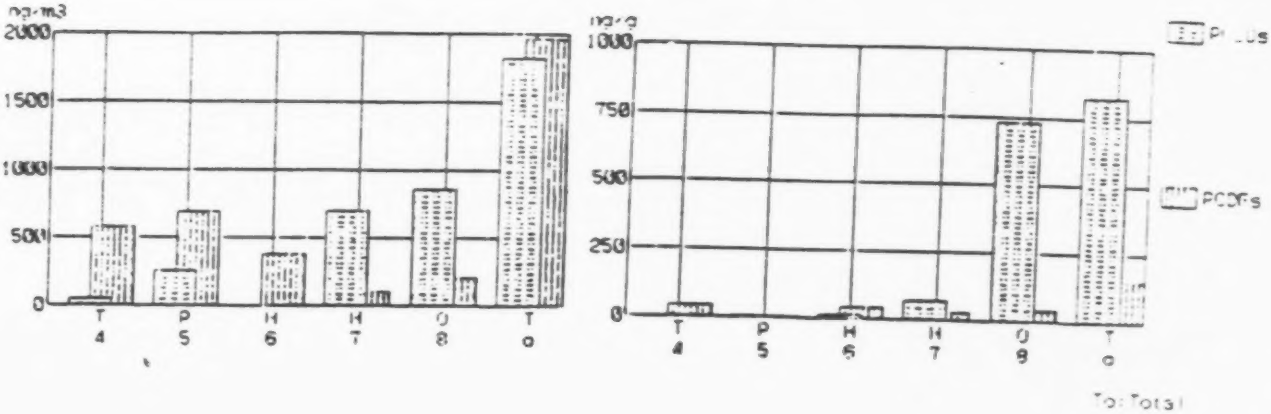


Figure 26: PCDD/PCDF in Exhaust Gas (left) and in Fly Ashes (right)

The average concentrations of PCDDs and PCDFs in the flue gas of 15 fully-continuous incinerators are shown in Figure 26 (left). The more chlorinated dioxins dominate the PCDD homologue distribution while the lower chlorinated furans, in particular the Cl_5DFs, dominate the PCDF distribution. These results are similar to those observed in other studies.

The average concentrations of PCDDs and PCDFs in the fly ashes of 19 fully-continuous incinerators are given in Figure 26 (right). The total amount of PCDDs produced on average is about four times the amount of PCDFs produced with Cl_8DD being by far the dominant species.

The incinerators studied were chosen from different districts in Japan. They were representative of the different types of incinerators and consequently were operated under various conditions. No conclusions could be drawn regarding the dependence of PCDD/PCDF formation upon operating conditions.

Reproduced from best avail

In 1985 two of the incinerators studied in the earlier survey were chosen for further investigation, primarily because of the high concentrations of PCDDs which were detected in their flue gases (Hiroaka et al., 1987). Incinerators A and B have the same capacity, 600 tons/day, but incinerator A uses a dry scrubber and electrostatic precipitator for pollution control whereas B uses a wet scrubber. The operating conditions for the two incinerators are given in Table XLVI. Flue gas, fly ash and discharged water were sampled, the results of the analyses are given in Tables XLVII-XLIX. The composition of the refuse as studied in 1984 and 1985 are shown in Table L. Figure 26 shows a comparison of the flue gas concentrations for both years. It should be noted that packed column GC/MS was used for determinations in the earlier study while capillary column GC/MS was used in the later analyses. Thus the first study gives much higher levels because interferences are undoubtedly present. For incinerator A, it appeared that whenever the PCDD content of the fly ash was high, the flue gas levels were low. Similarly, high flue gas PCDD content usually corresponded to low levels present in the fly ash. The concentration of PCDDs in the flue gas exiting the wet scrubber appeared to higher than for the dry scrubber, however the latter system had higher amounts of PCDDs in its fly ash. The effects of refuse composition could not be determined from the data collected.

Table XLVI: Operating Conditions of Municipal Waste Incinerators A and B

		Incinerator A			Incinerator B		
		2/4	2/5	2/6	2/18	2/19	2/20*
Incinerated Amounts	per hour	6.82	6.53	6.91	8.88	9.13	8.79
	per day	163.7	156.8	156.8	213.2	219.0	211.0
Temperature of Incinerator (°C)	Average	690	683	725	890	880	900
	Max.	811	812	794	1110	1040	1080
	Min.	607	503	611	740	660	700
Inlet Gas Temp. of Ep (°C)	Average	297	295	309	—	—	—
	Max.	330	338	339	—	—	—
	Min.	254	254	276	—	—	—
Exhaust Gas Volume KNm^3/h	Average	43.3	42.4	42.8	52	54	55
	Max.	57.3	54.1	58.0	72	68	68
	Min.	36.0	33.6	35.2	43	43	44
$HC\ell$ Concentration (ppm)	Average	313	334	343	0.5	0.3	0.4
	Max.	497	636	572	5	20	7
	Min.	176	146	203	0	0	0
O_2 Concentration (%)	Average	14.1	14.1	13.7	9.8	9.3	11.1
	Max.	15.7	17.2	15.6	12.8	13.2	15.0
	Min.	12.6	11.8	11.9	6.8	7.5	9.2

Table XLVII: Analyses of Flue Gas (Exhaust Gas) [ng/Nm^3]

	Date	samples	T$_4$CDD	P$_5$CDD	H$_6$CDD	H$_7$CDD	OCDD	PCDDs	2,3,7,8-T$_4$CDD
Incinerator A	2/4	1	12	70	225	570	1000	1900	< 0.69
		2	13	89	290	420	760	1600	< 1.08
		3	< 3	31	580	1100	1700	3400	—
	2/5	1	75	67	450	850	2200	3600	< 0.54
		2	7	5	11	28	62	110	< 1.07
		3	83	310	600	720	1200	2900	—
	2/6	1	96	740	2800	4500	6600	14700	3.7 Particulate matter 2.0
		2	24	140	580	1500	1300	3500	—
		3	19	100	1000	2400	4400	7900	—
Incinerator B	2/18	1	8.6	49	200	470	920	1600	< 0.17
		2	4.2	62	17	340	1500	1900	1.5
		3	5.3	19	11	140	400	580	—
	2/19	1	5.3	< 2	< 3	130	460	590	Particulate matter < 0.19 Gas < 0.10
		2	< 1	< 2	< 4	56	190	250	—
		3	8.3	12	12	100	250	380	—
	2/20	1	< 1	18	< 3	25	93	140	< 0.69
		2	8.0	< 2	13	37	100	160	< 0.52
		3	1.5	< 3	< 3	57	160	220	—

Table XLVIII: Analyses of Fly Ash [ng/g]

	Date	Samples	T$_4$CDD	P$_5$CDD	H$_6$CDD	H$_7$CDD	OCDD	PCDDs	2,3,7,8-T$_4$CDD
Incinerator A	2/4	1	2.8	9.8	25	22	31	91	0.77
		2	3.1	11	14	11	43	82	0.32
		3	1.6	1.7	7.9	8.9	7.2	27	—
	2/5	1	3.1	14	28	22	16	83	0.53
		2	12	45	91	64	37	250	0.56
		3	5.8	1.9	29	24	18	79	—
	2/6	1	4.3	16	37	20	37	110	1.06
		2	7.8	50	66	55	33	220	—
		3	12	64	71	60	41	230	—
Incinerator B	2/18	1	1.5	3.5	2.9	2.3	3.0	13	0.40
		2	0.3	0.9	3.4	7.9	13	28	0.12
		3	< 0.1	< 0.1	0.2	0.7	1.6	2.5	—
	2/19	1	0.4	0.2	0.6	0.9	2.6	4.7	< 0.02
		2	0.2	0.9	2.0	2.1	3.8	9.0	—
		3	0.4	0.8	1.2	2.6	10	15	—
	2/20	1	2.9	4.2	16	12	6.6	42	< 0.01
		2	0.1	0.2	1.4	3.9	12	18	0.12
		3	0.2	0.8	0.9	1.3	2.8	6.0	—

Table XLIX: Analyses of Discharged Water [ng/L]

	Date	Samples	T.CDD	P.CDD	H.CDD	H.CDD	OCDD	PCDDs	2.3.7.8-T.CDD
Incinerator A	2/6	1	< 0.05	< 0.1	< 0.08	< 0.03	< 0.2	< 0.46	< 0.08
Incinerator B	2/19	2	< 0.05	< 0.1	0.36	0.79	1.9	3.0	< 0.08

Table L: Composition of Municipal Waste
[Unit: %;Caloric Value: kcal/kg]

Incinerator / composition of Refuse	A		B	
	Average in 1984	Average in 1985	Average in 1984	Average in 1985
Water	45.5	24.3	47.7	13.5
Ash	14.8	20.1	13.2	21.2
Combustible Material	39.7	55.6	39.1	65.3
Paper · Textile	41.2	60.4	26.3	43.9
Wood · Bamboo	4.9	1.4	1.3	15.7
Plastics	20.2	17.8	16.0	18.9
Garbage	7.8	2.3	42.7	2.3
Uncombustible Material	21.6	16.6	10.7	15.4
Others	4.3	1.5	3.0	3.8
Low Calorific Value	1794	2830	1816	3536

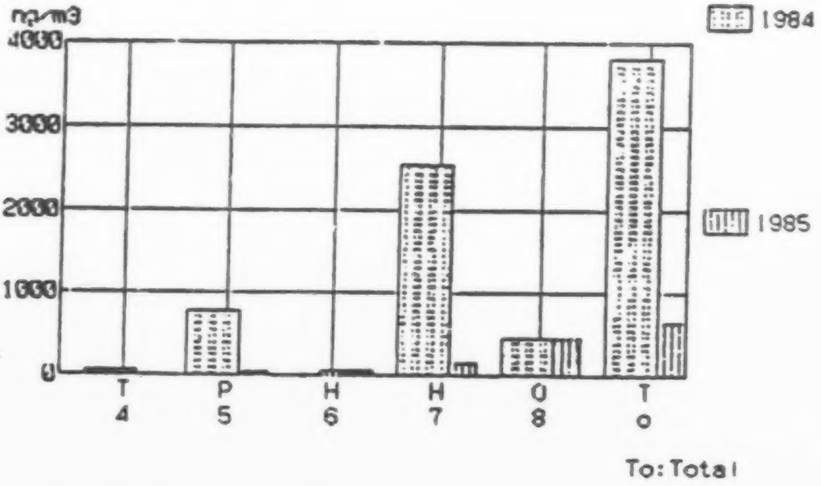


Figure 27: PCDD in Flue Gas; Comparison of two Years

In another Japanese study, fly ash, bottom ash, flue gas, and atmospheric samples were collected and analyzed for four incinerators from different locations (Asada et al., 1987). Two of the incinerators studied were operated under continuous flow conditions while the others were batch incinerators. A curious choice of standards were selected to test the flue gas and atmospheric gas sampling devices. Di-, tri-, and tetra-CDD isomers were used for recovery studies, yet the analyses involved the tetra- through octa-CDD compounds only. Good recoveries were observed, however such information would be more encouraging if similar recoveries were shown for the higher chlorinated species. The average results of the levels determined for the four Japanese municipal waste incinerators are given in Table LI. The isomer patterns for each type of sample were found to be quite similar.

Table LI: Concentrations of PCDD and PCDF in Municipal Waste Incinerators

	Fly Ash [ng/g]	Bottom Ash [ng/g]	Flue Gas [ng/m^3]	Atmosphere [pg/m^3]
	Min - Max (Ave)	Min - Max (Ave)	Min - Max (Ave)	Min - Max (Ave)
2,3,7,8-Cl_4DD	N.D.-5.01 (1.05)	N.D. N.D.	0.28-1.20 (0.67)	N.D. N.D.
Cl_4DD	1.30-220 (62.3)	0.15-0.99 (0.48)	0.66-175 (53.6)	N.D.-4.9 (4.3)
Cl_5DD	N.D.-121 (79.1)	0.20-155 (1.00)	4.05-164 (66.0)	N.D.-2.0 (2.0)
Cl_6DD	N.D.-279 (121)	2.53-6.69 (4.66)	22.4-188 (101)	N.D.-16.8 (11.9)
Cl_7DD	14.9-427 (186)	3.16-15.9 (6.53)	30.8-249 (148)	N.D.-35.1 (18.9)
Cl_8DD	7.80-527 (249)	1.12-18.4 (6.44)	19.6-264 (114)	N.D.-27.2 (10.8)
Total CDDs	80.5-1250 (624)	9.25-43.1 (19.1)	101-924 (527)	N.D.-86.2 (26.8)
Cl_4DF	3.24-237 (66.7)	0.11-0.76 (0.44)	33.6-152 (84.5)	---
Cl_5DF	2.08-262 (80.4)	0.15-3.23 (1.07)	61.3-227 (145)	---
Cl_6DF	20.2-373 (107)	0.07-1.03 (0.52)	67.1-229 (180)	---
Cl_7DF	1.70-519 (117)	0.07-0.79 0.32)	27.1-109 (66.8)	---
Cl_8DF	5.83-441 120	N.D.-0.99 (0.40)	8.64-58.7 (34.0)	---
Total-CDF	22.4-1,510 (491)	0.62-5.89 (2.74)	231-761 511)	---

3.4 Municipal Waste Incineration in Denmark

There are currently 45 municipal waste incinerators operating in Denmark, most of which are equipped with boilers for heat production (Bendixen and Nielsen, 1987). Approximately 50% of the total municipal refuse is burned in these incinerators.

Figure 28 shows the ratio of remaining concentration at time t = 2 seconds, C_t, to the initial concentration, C_o, for the thermal treatment of biphenyl, carbon monoxide (CO), and PCDD. CO has a high thermal stability (destroyed at temperatures greater than 827 °C), but PCDD has even higher stability since temperatures greater than 1,017 °C are required for destruction at a 2 second reaction time. Thus low CO emission can be considered as a prerequisite (but not an indicator) for low PCDD emission

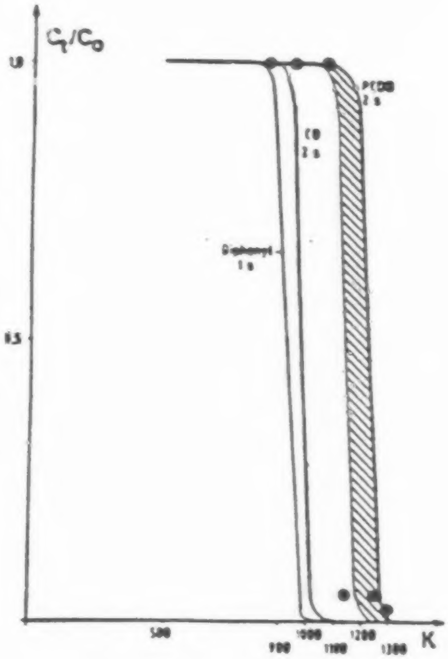


Figure 28: Ratio of Biphenyl, Carbon Monoxide, and PCDD after Thermal Treatment

A Copenhagen incinerator equipped with refractory lined furnace, rotary kiln, and burn-out chamber was studied in an attempt to correlate PCDD emission levels with burn-out temperature (Bendixen and Nielsen, 1987). The 12 tons/hour incinerator used an energy recovery boiler and electrostatic precipitator for cooling and cleaning respectively of the flue gas.

The total concentration of PCDDs and PCDFs as a function of the burn-out temperature is shown in Figure 29.

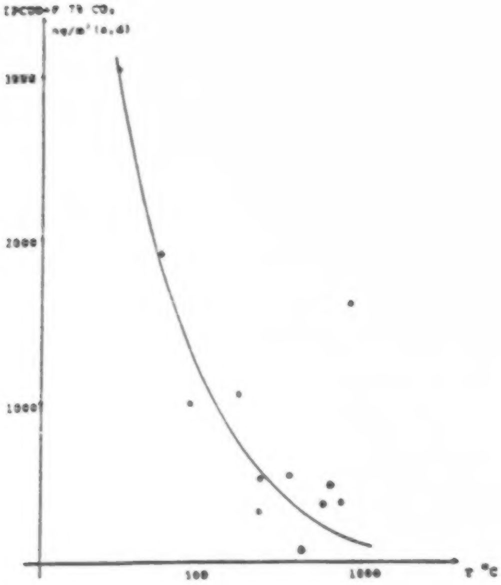


Figure 29: PCDD and PCDF Concentrations as Function of Burn-out Temperature

The relationship between PCDD/PCDF and CO emissions was investigated for the Copenhagen incinerator and two smaller incinerators having capacities of 3.0 and 3.5 tons/hour. The smaller incinerators both had refractory lined furnaces and burn-out chambers, heat recovery boilers, and electrostatic precipitators for flue gas cleaning. The total PCDD/PCDF concentration versus the concentration of CO emitted for all three incinerators is given in Figure 30. As predicted, the lowest PCDD/PCDF concentrations were found for low CO concentration and high combustion temperature.

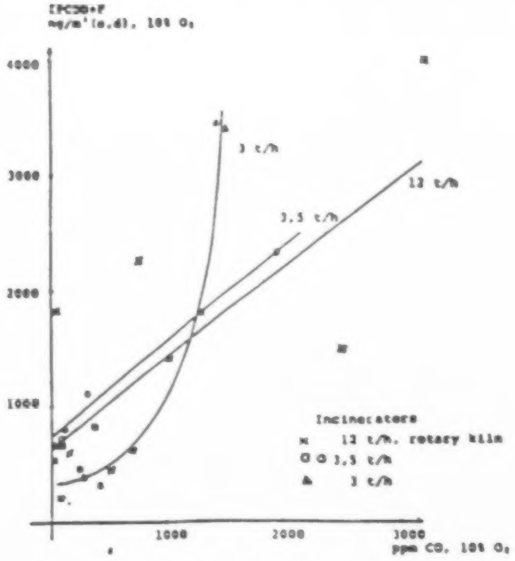


Figure 30: Relationship between PCDD- and CO-Concentration for Three Incinerators

Guidelines for efficient incineration and reduced PCDD/PCDF emissions were suggested by the Danish EPA:

1. Preheat combustion air
2. Have a support burner
3. Refractory lining of furnace and burn-out chamber
4. Minimum 2 second dwell time in burn-out chamber
5. No CO gradient in burn-out chamber
6. Maintain burn-out chamber at 950 °C
7. Start support burners if burn-out temperature drops to 875 °C
8. Burn-out chamber temperature must be maintained at greater than 875 °C for 95% of the time without support burners in operation
9. Feeding of waste stopped when burn-out chamber temperature drops below 825 °C
10. Continuous monitoring and control of combustion process.

3.5 Municipal Waste Incineration in Sweden

Municipal waste incinerators operated in Sweden were studied (Tysklind et al., 1987) . Variations in total emissions were observed, however the patterns of isomers found for individual PCDD and PCDF homologues were found to be similar even for incinerators producing relatively high and low emissions (see Figure 31). The PCDD and PCDF congener profiles for three Swedish municipal waste incinerators are shown in Figure 32. The relative distributions were very similar even though the total levels were different. The highest PCDF emissions were found to be due to the Cl$_4$DFs and Cl$_5$DFs while Cl$_5$DDs dominated in the levels of PCDDs present.

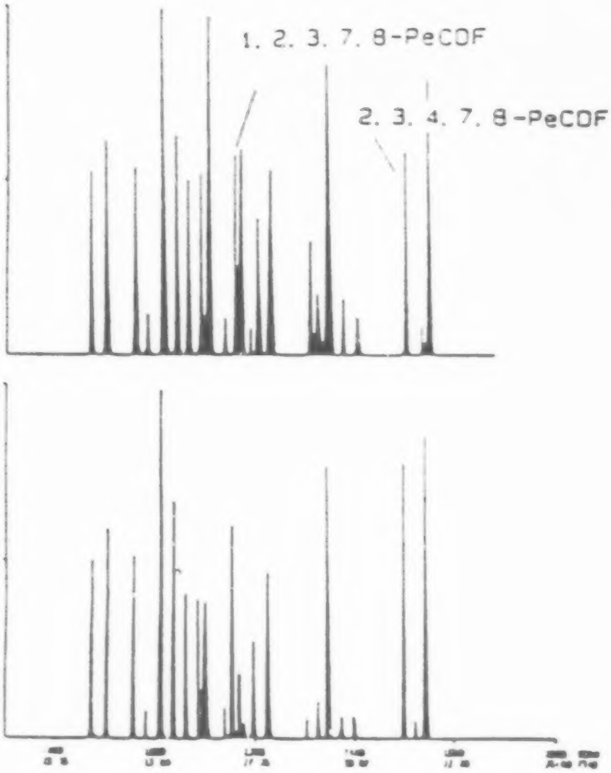


Figure 31: Cl$_5$DFs in Emissions from Two Different Municipal Waste Incinerators

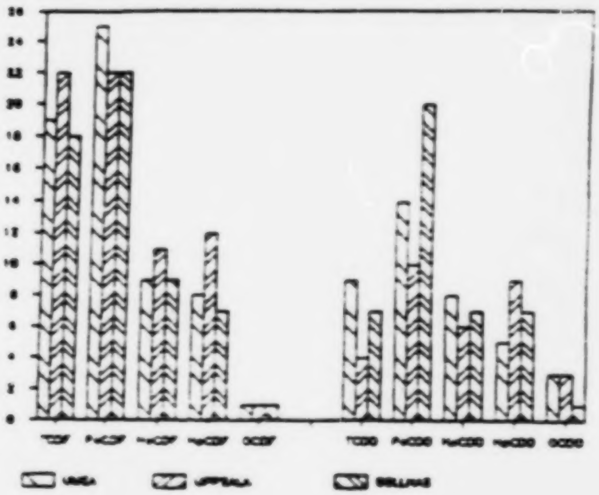


Figure 32: Congener Profile of PCDD and PCDF in Emissions from Three Swedish Municipal Waste Incinerators

All Swedish waste incinerators are combined with energy production (Bergström and Warman, 1987). The energy produced is used mostly for district heating. During waste incineration, a very efficient oxidation of the organic substances takes place. The particle size of waste varies and there is big difference in composition. Usually, 2% of the organic matter in the waste leaves the furnace with the slag and fly ash. About 75% of the chlorine in the fuel occurs as HCl in flue gas. Less than 0.1% of the chlorine produces chlorinated aromatics. Polychlorinated dibenzodioxins and furans compride only a small part of the chlorinated aromatics that are produced. Authorities in Sweden have chosen to describe the emission by a weighted mean value of 12 isomers which are considered to be especially toxic according to a model developed by Eadon (Eadon et al., 1983). The "TCDD" equivalents released with the flue gases from different incinerators amount between 1 and 50 ng/m^3 of flue gas. Taking into account the uncertainty of the method of measurement, the differences are very small. The incineration conditions have a greater influence on the emission of many other organic trace pollutants, such as polycyclic aromatic hydrocarbons, than on PCDD/PCDFs.

Reproduced from
best available copy

As PCDD/PCDFs are present on dust particles and emitted with the fly ash to a much higher degree than many other compounds formed during the combustion, the emission of PCDD/PCDFs can effectively reduced by an efficient flue gas cleaning system. However, flue gas cleaning does not reduce the quantity of pollutants fed with the wastes or formed in the incinerator.

In Sweden, measurement were carried out on several municipal waste heating plants using the same sampling and analytic methods on each plant. Operational studies for characterization of firing conditions have been reported elsewhere (Bergström and Warman, 1987). Parameter of furnace load were calculated; furnace temperature, flow and distribution of combustion air were measured; slag and fly ash were checked during the test. Gases emitted (excess oxygen, carbon dioxide and carbon monoxide) were monitored continuously and stored in a computer, as average values for five minutes. The sampling system for organic micro-pollutants was described (Bergvall and Hult; Öberg et al., 1985). Dioxins and related compounds were determined after clean up on aluminia according to Buser (Buser, 1975) and analyzed by GC/SIM. The results are given in Table LII.

Table LII: Organic Micro-pollutants in the Flue Gas Samples
Operation with a Large Excess of Oxygen
[μg/standard m^3] corrected to 10% CO_2

	Test	
	1	2
CE	99.80	99.85
CE	99.64	99.78
Total organics (RI > 900)	140	100
Total PAH	1.3	0.5
Total chlorobenzenes	17	8.0
Hexachlorobenzene	5.3	2.6
Total chlorophenols	25	8.0
Pentachlorophenol	1.3	0.7
Total TCDD	1.9	0.9
2,3,7,8-TCDD	0.5	0.2
Total PeCDD	18	6.9
1,2,3,7,8-PeCDD	1.2	0.6
Total TCDF	38	15
2,3,7,8-TCDF	3.8	1.9
Total PeCDF	58	25
1,2,3,7,8-PeCDF	7.1	3.5
TCDD equivalents (Eadon)	7	4

The test results from different plants show that three factors are of great importance when limiting the production of organic micro-compounds in the furnace and the boiler. Combustion efficiency (CE) is the most important factor influencing the production of all kinds of aromatic compounds in the flue gas. Combustion efficiencies CE > 99.9%, i.e. 100 ppm CO adjusted to 10% CO_2, are considered to be a high combustion efficiency for ordinary grate fired units. During such operation conditions the frequency of CO peaks has a great influence on the production of aromatic compounds, including PCDD/PCDFs. Table LIII shows the influence of CO peaks on the production of TCDD-equivalents in another waste heating plant equipped with a high efficiency flue gas cleaning. The values in Table LIII represent PCDD/PCDF concentrations after the boiler but before flue gas cleaning. After cleaning the emission of TCDD-equivalents with the flue gas was less than 0.1 ng/m^3 at 10% CO_2 in all four tests. From Table LII it might be seen that test 2 gives lower concentrations of all compounds in the flue gas. During test 2 there was no five-minute period with CE lower than 99.78%.

Table LIII: Influence of Combustion Efficiency on the Production of TCDD-Equivalents

Number of five-minute Periods with CE<99.9% during Sampling	TCDD-Equivalents [ng/m^3]
9	44
4	9
2	3
0	2

The results show a co-variation of different aromatic micro-pollutants produced in the furnace and the boiler. Seven tests in one incinerator show that combustion conditions which results in small amounts of PCDD/PCDFs also produce low concentrations of PAH and the chlorobenzenes. The chloride concentrations in the flue gas after the boilers have certainly been in the range 600-1,000 mg/m^3 at 10% CO_2 calculated as HCl.

It was possible to make good prediction of the chlorinated micro-pollutants present in the flue gas using the factors CE and HCl content. A third factor that was found to be important was excess air, measured as O_2, in the flue gas. However, because CE and O_2 content are highly correlated in the range 5-12% O_2, either one could be used to predict the production of chlorinated aromatic pollutants.

3.6 Waste Incineration in the United Kingdom and Scotland

In the years 1985/86 four commercially available merchant high-temperature incinerators were in operation in U.K.; these plants were at Ellesmere Port, Pontypool, Fawley, and Hucknall (Hazardous Waste Inspectorate, 1986). Together they represent a notational installed capacity of some 61,000 tons per annum, of which approximately 6,000 tons are available for solid wastes and the balance for liquids. Additionally, the in-house incinerator operated at West Bromwhich takes in certain liquid combustible wastes on a commercial basis and represents a further 4,000 tons per year of liquid waste incineration capacity. There are currently 60 in-house chemical waste incinerators registered under the Health & Safety (Emissions into the Atmosphere) Regulations 1983. These plants are, in main, integral with chemical process plant and, therefore, not subject to disposal site licensing under the Control of Pollution Act 1974.

Perhaps the most significant current development in high-temperature incineration is the apparent increase in the use of marine incineration by U.K. waste producers. The trend in utilisation of this disposal route is upward from 811 tons in 1981 to an estimated 3,500 tons in 1984. The actual tonnage of UK hazardous waste incinerated at sea during 1984 was 1,952 tons, only 26% of the licensed quantity, and a reduction from the 1983 total. During 1985, however 2,584 tons of UK wastes were incinerated at sea, and 7,850 tons are licensed for marine incineration during 1986.

Analytical results of PCDD/PCDF analyses have not been published due to lack of suitable analytical standards and to limitations in the analytical method employed. UK claims to develop standard methods of extraction, separation and analysis of PCDD/PCDFs.

In Scotland the total amount of waste is quantified to about 4.5 million tons: household waste arisings are about 1.8 million tons per annum (ca. 40%), the other 2.73 million tons (ca. 60%) are commercial and industrial arisings. Most of the household waste and some of the commercial and industrial waste are disposed of at local authorities operated landfill sites to the amount of approximately 2.8 million tons per annum in all. Of the rest about 200,000 tons per annum are incinerated to atmosphere by waste disposal authorities (1.5 million tons are disposed of at landfill sites operated by private sector contractors). In 1983-4 there were 11 municipal waste incinerators operating, which disposed of some 250,000 tons; in December 1985 only 10 plants operated about 200,000 tons of waste. Incineration by these municipal waste incinerators produces gaseous emissions to the atmosphere, almost entirely of carbon dioxide. However, in Scotland, only one major incinerator has been commissioned in the past decade.

The only incineration facility for the specific disposal of wastes containing PCBs has been closed in 1984.

In future, more information has to be obtained on the impact of dioxins and furans to the environment.

3.7 Resource Recovery in the United States

The solid waste disposal crisis, which arose as the result of landfills being filled to capacity and a shortage of land for new sites near expanding urban areas, has generated an increasing interest of cities throughout the United States and the world to invest in various of resource recovery. Alternative solutions to the crisis include recycling and waste reduction and large-scale energy and materials recovery facilities (known as resource recovery and RDF, respectively). The discovery of dioxin and furan emissions from resource recovery plants has led to an intensive focus on the dioxin issue by the public, the regulators, and the builders of the plants.

Mass burning, a technology perfected in Europe for energy recovery, is used in numerous plants now operating in the United States. Most of the mass burn plants create steam for district heating loops and fir industrial processes; a few generate electricity. There are other plants which employ a variety of separation and Refuse-Drived Fuel (RDF) preparation technologies. Whilst many of the facilities in the U.S.A. will process only relatively small quantities of refuse (less than 500 tons per day), approximately 40% of the plants will process sewage sludge in addition to garbage. A number of usable products, including pelletized and fluff refuse-derived fuel for different uses, ferrous metals, aluminium, chilled water, glass, methane gas, carbon monoxide, humus, compost, and corrugated and baled paper. Most plants have been constructed in urban centers and dispose of municipal waste, but some have been built on army and navy bases and on college campuses (Steisel et al., 1987).

Due to the paucity of usable data from operating resource recovery plants (i.e. complete combustion information and dioxin samples taken over periods of time during which combustion conditions are held constant) the American Society of Mechanical Engineers (ASME) has developed a proposed protocol which is now under review. The New York Department of Environmental Conservation researches at sic resource recovery plants of different design. Another testing program of the ASME was established for the purpose of conducting combustion research at a number of facilities to learn the effects of varying refuse composition (i.e. moisture, PVC content) on emissions of dioxins and related compounds. Dioxin testes were funded by a number of Satas, i.e. New York, Florida, California, Massachussetts and others.

3.8 Influence of the Type of Refuse

A study of the influence of the type of refuse material was recently reported in which sorted and unsorted refuse were burned in a municipal incinerator (Benfenati et al., 1986). Table LIV gives the average compositions of the waste combusted in the tests. The results of the study are listed in Table LV. No conclusions were made regarding the effect of the refuse on the emissions of PCDDs and PCDFs. Considerable variation in the resulting levels were observed , however there does not appear to be any relationship to the nature of the refuse burned. High moisture levels in the refuse result in lower combustion temperatures and consequently in higher emissions of PCDDs and PCDFs.

Table LIV: Composition of Combusted Waste

Parameter	Original Waste (%)		Processed Waste (%)	
	Weight	Moisture	Weight	Moisture
Paper	23.0	40	7.2	60
Soft plastics	7.6	---	11.0	---
Hard plastics	4.8	---	12.1---	
Cloth	3.6	15	8.8	76
Wood	1.6	12	5.1	15
Inert material	5.7	---	3.1	---
Organic material	30.7	57	15.0	37
Iron	4.5	---	9.3	---
Material smaller than 20 mm	18.5	58	28.4	67
Moisture	37.6	36.5		
Cinders	32.9	26.5		

Table LV: Cl_4DD and Cl_4DF [ng/Nm^3] in the Condensate before the Abatement System (upstream) and the Stack (downstream)

Sample number	Kind of refuse	TCDD		TCDF	
		upstream	downstream	upstream	downstream
1	Processed	23.6	13.3	60.8	3.1
2	Processed	<3.0	1.9	51.9	9.1
3	Unprocessed	22.7	1.2	31.7	8.0
4	Unprocessed	16.9	2.3	52.0	5.2
5	Processed	13.0	5.2	81.5	17.0
6	Processed	9.1	2.5	49.0	6.0
7	Processed	68.0	20.9	195.0	65.0
8	Processed	79.5	9.6	275.0	42.2

Table LVI summarizes the PCDD emission data taken from municipal incinerators from throughout the world (Jones et al., 1986). The total levels of PCDDs emitted are found to span a very wide range of values. Contrary to what was concluded from the National Dioxin Study conducted by the U.S. EPA (des Rosiers, 1987), the plants equipped for heat recovery show low emissions as compared to other incinerators not equipped in this way. This list is not comprehensive but includes plants for which better documented studies have been performed. According to this collection of data:

1. Plants with energy recovery on average have about one-tenth the PCDD/PCDF emissions of those without energy recovery equipment;
2. The majority of the emissions for energy recovery plants are PCDFs;
3. The level of 2,3,7,8-Cl_4DD is very small relative to the total PCDD/PCDF emissions;
4. Tetra-CDFs are the dominant homologue in the resource recovery emissions.

A more comprehensive list of results (although comprised of mainly earlier incinerator studies) was compiled in a study concerned with the sources and levels of PCDDs and PCDFs entering the environment (Ontario Ministry of the Environment, 1985). The results of the literature survey are summarized in Tables LVI to LVIII. The results within these tables were averaged and are reported in Table LXIX, along with the number of values averaged and the calculated standard deviations of each average. The standard deviations are always larger than the averages themselves which indicates the great variation of the reported levels of PCDD and PCDF emitted by municipal waste incinerators.

Table LVI: Distribution of Worldwide PCDD Emissions Data (tetra through octa Congeners) [ng/Nm^3, dry]

Facility	Country	All data	Plants with Heat Recovery	Best data
Montreal (Des Carrieres)	Canada	<1	<1	
Westchester RESCO	USA	24	24	
Würzburg	FRG	25	25	25
Pittsfield (Vicon)	USA	37	37	37
Chicago, NW	USA	44	44	44
Stapelfeld	FRG	49	49	49
Eksjo	Sweden	70	70	70
PEI	Canada	107	107	107
Stellinger Moor	FRG	130	130	130
Zürich	Switzerland	131	131	131
Borsigstrasse	FRG	172	172	172
Albany RDF (Sheridan Ave)	USA	310	310	310
Valmadiera	Italy	310		
Italy 1	Italy	516		
Italy 6	Italy	675		
Italy 5	Italy	746		
Niagara RDF (Occidental Chemical Co.)	USA	827	827	827
Zaanstad	Netherlands	1,294		
Hamilton/ Wentworth SWARU	Canada	4,332	4,332	
Italy 4	Italy	5,003		
Toronto	Canada	5,086		
Hampton (Langley Field)	USA	5,395	5,395	
Italy 3	Italy	8,622		
Italy 2	Italy	33,047		

eproduced from
st available copy

Table LVII: Levels of PCDD/PCDF in Precipitated Fly Ash from Municipal Waste Incinerator Plants [ng/g]

erence	Location	Sampling Interval	PCDD						PCDF						Total PCDD + PCDF
			T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total	
r & Bosshardt 978)	Switzerland (Zurich)	1 plant	2	8	30	60	120	220	1	4	30	40	10	85	305
man et al. 9),(1980)	Canada (Ontario)	2 plants	12.0 9.3	15	13	3	0.4	41							
	Japan	2 plants	4.8 8.5												
	The Netherlands	1 plant	2.4												
llaro l. (1980)	Italy	4 plants	6.1 1.1 0.1 2.7				150 36 0.7 166						166 22 0.2 70		
araki & rick 980)	U.S.A.	1 plant	7.8		14	28	30	(72)*							
	Europe	1 plant	69.7		550	1040	650	(2310)*							
enhauwer l. (1980)	The Netherlands	1 plant - Ave. of 1/wk for 4 wks	58	192	375	363	135	1123	94	192	336	218	22	862	1985
man et al. 981)	Canada (Ontario)	1 plant Ave. of 1/wk for 8 wks	13.5	23.2	25.8	14.9	6.3	84							
e (1981)	Germany	1 plant	25												
llaro l. (1982)	Italy	5 plants	0.25 0 46.4 0.7 0	1.7 0.92 65.4 0.05 0	294 1.8 2496 0.02 0	8.9 3.1 87.9 0.007 0.0012	295 1.5 841.5 0.1 5.86	600 7 3537 1 6	0.46 0.8 61.7 1.88 0				15.8 3.3 255 0.002 1.93		

Table LVII continued:

eference	Location	Sampling Interval	PCDD						PCDF						Total PCDD + PCDF
			T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total	
ement & Karasek (1982)	Canada (Ontario)	1 plant-Ave. of 2 days	5.0	4.9	4.2	2.5	5.3	22							
berti *et al.* (1982)	Italy	4 plants	2.7 85 49 4	7.4 165 33 108	21 595 14 4	47.1 835 6 11	92 520 2.7 5	170 2200 105 152	10.4 285 576 247	29.5 415 216 358	37 910 57 91	50.5 715 13 34	15 125 15 3	142.4 2450 877 735	313 4650 982 887
ie *et al.* (1982)	The Netherlands	9 plants	101 13 24 226 212 0 40 18 373		310 250 136 560 910 10 330 140 1340		40 1370 51 110 550 10 190 190 990		230 90 91 240 220 50 110 70 430		230 230 82 280 530 60 150 70 1200		0 90 11 10 110 10 40 20 140		
llschmiter *al.* (1983)	W. Germany	6 plants					0.5 1 13 15 520								
ment *et al.* (1983)	Canada (Ontario)	1 plant Ave. of 8 days	26	29	20	7	13	95							
	Canada (Ontario)	1 plant Ave. of 1/hr over 5 hrs.	28	30	22	8	14	102							
rasek & Viau (1983)	W. Germany	1 plant Ave. of 3 mos.	0	0	0.3	1.2	11.8	13	9.9	2.9	3	3.8	4.9	24.5	38
le *et al.* 983)	The Netherlands (Alkmaar)	1 plant Ave. over 17 mo.	114	205	435	247	96	1097	220	304	421	206	18	1169	2266

Table LVII continued:

aference	Location	Sampling Interval	PCDD						PCDF						Total PCDD + PCDF
			T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total	
ie et al. 1983) (Cont'd)	The Netherlands (Amsterdam)	1 plant Ave. over 18 mo.	14	39	126	202	401	782	62	62	128	82	33	367	1149
	The Netherlands (Zaanstad)	1 plant Ave. over 2.5 hr.	89	434	1522	1702	974	4721	183	399	863	542	94	2081	6801
	The Netherlands (Zaanstad)	1 plant Ave. over 21 mo.	107	310	731	687	359	2194	211	367	590	395	60	1623	3817
vacic et al. (1984a)	Canada (Ontario)	1 plant 13 tests over 2 mos.	3.7	6.4	9.1	2.3	1.5	23	12	17	14	2.9	0.3	46	69
vacic (1985)	Canada (Ontario)	2 plants Ave. of 3 tests over 2 wks.	2120 30	1924 34	7124 80	2980 25	1015 9	15163 178	663 53	1007 59	2285 112	1178 21	118 7	5251 252	20414 430

Excludes P_5CDD

Reproduced from best available copy.

Table LVIII: Levels of PCDD/PCDF in Stack-Collected Particulates from Municipal Waste Incinerator Plants [ng/g]

eference	Location	PCDD						PCDF						Total PCDD + PCDF
		T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total	
tenhouwer *et al.* (1982)	The Netherlands)	100	800	1370	1370	310	3950	460	960	1600	1130	140	4290	8240
ttle (1981)	Germany	300												
erti & Brocco (1982)	Italy (Florence)		80	180	290	510	(1060)*				110	60		1230
iu *et al.* (1983)	Canada	10 0	269 168	390 173	11 127	8 1	688 469	46 279	153 265	1712 392	47 104	0 0	1958 1040	2646 1509
vacic *et al.* 984a)	Canada (Ontario)	2100	2300	2900	1700	1900	11000	8500	8000	4600	1400	370	23000	34000

Excludes T_4CDD

Table LXIX: Levels of PCDD/PCDF in Stack Emissions from Municipal Waste Incinerator Plants [ng/g]

ference	Location	Sample Type*	PCDD						PCDF						Total PCDD + PCDF	** Units
			T4	P5	H6	H7	O8	Total	T4	P5	H6	H7	O8	Total		
allaro al. (1980)	Italy (Zanu - Milan)	P	3				290						37			
		G	19				732						675			ng/Nm³
		T	22				952						712			
	Italy (Busto Arsizio)	P	0.6				37						70			
		G	0.8				11						10			
		T	1.4				48						80			
ing & adskog 82)	Sweden	T (3 temp. regimes)			5 100 40	13 800 30	20 1000 300									ng/Nm³ NTP
llaro al. (1982)	Italy (6 plants)	P	1.1	2.7	11.5	1.0	8.0	24.3	ND				2.2			
		G	19.6	27.9	178.2	159.6	63.9	449.2	ND				59.3			ng/Nm³
		T	20.7	30.6	189.7	160.6	71.9	473.5	ND				61.5			
		P	172.2	172.3	12015	575	7312	20247	75.0				2883			
		G	17.0	107.0	26620	828	1179	28751	108.6				4390			ng/Nm³
		T	189.2	279.3	38635	1408	8491	49003	183.6				7273			
		P	0.04	0.3	6.7	0.2	1.7	8.9	2.6				0.1			
		G	19.0	40.0	6542	124.0	776.0	7501.0	429.0				1010.0			ng/Nm³
		T	19.0	40.3	6549	124.2	777.7	7509.9	431.6				1010.1			

duced from
vailable copy.

Table LXIX continued:

eference	Location	Sample Type*	PCDD						PCDF						Total PCDD + PCDF	** Units
			T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total		
avallaro t al. (1982) Cont'd)	Italy (6 plants) (Cont'd)	P G T	10.9 60.0 70.9	2.8 33.0 35.8	0.5 1390.0 1390.5	3.2 167.0 170.2	39 2703 2742	56.4 4353.0 4409.4	3.7 1814.0 1817.7				0.1 1760.0 1760.1			ng/Nm^3
		P G T	0.3 9.6 9.9	2.4 21.0 23.4	196 328 524	9.9 46.0 55.9	173 244 417	381.6 648.6 1030.2	75.3 305.0 380.3				3.2 89.0 92.2			ng/Nm^3
		P G T	ND 19.0 19.0	0.01 11.0 11.01	0.3 480.0 480.3	ND 6.0 6.0	0.5 71.0 71.5	0.8 587.0 587.8	ND 27.0 27.0				ND 24.0 24.0			ng/Nm^3
izzi et al. 1982)	Italy (como)	T- Ave. over 9 months	130	199	366	286	126	1107	309	250	314	215	124	1212	2319	ng/Nm^3
berti & Brocco 1982)	Italy (Florence)	P G													1570 261	ng/m^3
lie et al. 1982)	The Netherlands (Zaanstad)	P- Ave. over 7 months	57	231	440	347	452	1527	161	272	528	293	68	1322	2849	ng/Nm^3
OEP (1982)	Switzerland (Zurich - Josef-strasse)	P G T	3.4 0.6 4.0	9.9 1.1 11.0	22.7 2.2 24.9	22.1 2.0 24.1	47.5 1.1 48.6	106 7 113	15.5 66.8 82.3	19.9 7.4 27.3	14.3 4.4 18.7	9.7 2.7 12.4	7.7 0.5 8.2	67 82 149	173 89 262	ng/Nm^3
lie et al. 1983)	The Netherlands	T	25	85	211	194	166	701	65	141	242	161	84	693	1394	ng/Nm^3

Reproduced from best available copy

Table LXIX continued:

Reference	Location	Sample Type*	PCDD						PCDF						Total PCDD + PCDF	** Units
			T_4	P_5	H_6	H_7	O_8	Total	T_4	P_5	H_6	H_7	O_8	Total		
Ozvacic (1983)	Canada (Ontario)	T- Ave. of 3 tests	61	88	392	437	104	1082	226	177	365	245	72	1085	2167	ng/dscm
	Canada (Ontario)	T- Ave. of 3 tests	45	53	75	423	144	740	342	558	71	104	138	1213	1953	ng/dscm
	Canada (Ontario)	T- Ave. of 3 tests	4658	2543	454	319	67	8041	13231	6932	104	43	47	20357	28398	ng/dscm
Rappe et al. (1983a)	Sweden (Eksjo)	P	ND	ND	ND	20	13	33	37	10	25	25	9	106	139	ng/m³
		G	ND	ND	ND	7	4	11	68	6	10	7	1	92	103	
		T	ND	ND	ND	27	17	44	105	16	35	32	10	198	242	
		P	ND	ND	ND	12	10	22	25	4	4	8	8	49	71	ng/m³
		G	ND	ND	ND	25	8	56	525	87	80	15	6	713	769	
		T	ND	ND	ND	37	18	78	550	91	84	23	14	762	840	
Redford et al. (1983)	U.S.A.	T	6.3	NR	16	7.6	2.5	32.4 ***	90	NR	62	7.5	0.6	160.1 ***	192.5 ***	ng/dscm
Tiernan et al. (1983b)	U.S.A.	T	380	530	850	2000	490	4300	2600	1600	1800	2200	170	8300	12600	ng/m³
Ozvacic et al. (1984a)	Canada (Ontario)	P (Ave.	387	361	351	153	117	1369	1257	1110	520	103	29	3020	4389	ng/dscm
		G of 13	373	349	339	147	113	1321	1303	1150	540	107	31	3130	4451	
		T tests)	760	710	690	300	230	2690	2560	2260	1060	210	60	6150	8840	

P - particulate

G - gaseous

T - Total of particulates and gaseous data.

** 1 Nm^3 (normal cubic metre) = 0.925 dscm (dry standard cubic metre).

*** - Total PCDD/PCDF value excludes P_5CDD and P_5CDF.

Table LX: Summary of Average PCDD and PCDF Congener Concentrations and Calculated Total (Cl_4 - Cl_8) Values for Municipal Waste Incinerator Emissions

Matrix	Units**		PCDD						PCDF						Total* (T_4–O_8) PCDD + PCDF
			T4	P5	H6	H7	O8	Total* (T_4–O_8)	T4	P5	H6	H7	O8	Total* (T_4–O_8)	
- Weight Basis -															
Precipitated Fly Ash	ng/g	Ave.	90	151	528	322	227	1318	151	245	379	250	47	1072	2390
		n	44	24	35	26	45		28	14	23	14	32		
		s.d.	321	394	1265	680	344		172	271	527	348	61		
Stack-Collected Particulates	ng/g	Ave.	502	723	1003	700	546	3474	2321	2345	2076	558	114	7414	10888
		n	5	5	5	5	5		4	4	4	5	5		
		s.d.	901	925	1170	778	787		4123	3787	1786	653	154		
- Volume Basis*** -															
Stack-Collected Particulates	ng/m^3	Ave.	49	71	1186	104	654	2064	150	283	218	88	240	979	3043
		n	13	11	11	11	13		11	5	5	5	13		
		s.d.	112	126	3595	189	2005		370	476	279	121	795		
Stack-Collected Gaseous Phase	ng/m^3	Ave.	45	59	3588	151	492	4335	465	313	159	33	671	1641	5976
		n	12	10	10	10	12		10	4	4	4	12		
		s.d.	104	107	8334	247	798		615	560	257	50	1295		
Total Stack Emissions			338	290	2551	343	741	4263	1353	1205	378	296	618	3850	8113
	ng/m^3	n	19	16	20	20	22		17	10	11	11	19		
		s.d.	1062	635	8614	516	1835		3177	2151	558	638	1673		

[1] - from Tables 4.2.1.1A to 4.2.1.1C

* Total - Calculated from sum of average isomer group values.

** n. = number of values averaged.
s.d. = standard deviation.

*** - data for Nm^3 and dscm averaged without correction ($1Nm^3$ = 0.925 dscm).

**** - total of gaseous plus particulate phases.

III. SEWAGE SLUDGE INCINERATION

There are few reports of studies other than those done on municipal solid waste incinerators. In a recent study, the emissions of PCDDs and PCDFs were reported for a municipal sludge incinerator plant (Clement et al., 1987). Two twelve-hearth incinerators were tested. The top four hearths are used for drying the raw sludge (480-500 °C), the next four are used for incineration (700-800 °C), and the bottom hearths are used for burn-out and cooling (300-400 °C). The flue gas is cleaned by a scrubber and cooled using a sprayer system such that the scrubber exhaust gas temperature is 70 °C. Municipal sewage, which is 80-90% water, is delivered to the top hearth at a rate of 10 tons/hour.

Stack samples were collected with a modified EPA method 5 sampling train in which two florisil cartridges were placed in series after the third impinger. Samples recovered were collected as three fractions corresponding to the filter, impingers and florisil cartridges. Three separate tests (24 hour sampling) were done over a one week period. Raw sewage sludge and bottom ash were sampled periodically throughout each test in order to obtain composite samples representative of the 24 hour sampling time. All samples were fortified with ^{37}Cl-labelled octachlorodibenzo-p-dioxin before extraction.

Table LXI lists the concentrations of chlorinated organics, including PCDDs and PCDFs, which were found in the stack gases in the three tests. The levels of PCDDs and PCDFs found in the stack gases for the sewage sludge incinerator were found to be low in comparison to two municipal solid waste incinerators tested at about the same time using the same sampling method. Differences in the homologue distributions in the sewage and solid waste incinerators were found, however the effects of raw waste composition could not be determined. The significance of the quantitative data is difficult to assess due to the variations in the recoveries for each fraction. The average percent recoveries, shown in Table LXI, have uncertainties as large as the averages themselves. Recoveries were so low in some cases that the data were not even reported. The PCDD and PCDF concentrations were all corrected for recovery, however it is not clear how this correction was actually made.

Table LXI: Concentration of Chlorinated Organics in Sampling Train [ng/g]; dry Standard Conditions
LR: Low Recovery of isotopically labelled standard
ND:Not Detected

	TEST 1			TEST 2			TEST 3		
	filter	impinger	florisil	filter	impinger	florisil	filter	impinger	florisil
4CDD	LR**	11^{3}	ND	ND	5.4^{1}	ND	ND	14^{4}	LR**
5CDD	LR	ND	ND	ND	ND	ND	ND	1.5^{5}	LR
6CDD	LR	2.1^{2}	ND	ND	0.03^{2}	ND	ND	13^{3}	LR
7CDD	LR	8.0^{2}	1.8^{1}	7.3^{2}	0.7^{2}	0.7^{1}	ND	24^{2}	LR
8CDD	LR	4.6	1.2	ND	5.0	0.5	2.8	10	LR
4CDF	LR	35^{9}	2.7^{13}	ND	16^{11}	16^{12}	ND	33^{12}	LR
5CDF	LR	13^{2}	ND	1.7^{2}	7.9^{7}	2.7^{2}	ND	30^{8}	LR
6CDF	LR	ND	ND	ND	0.6^{2}	ND	ND	4.3^{4}	LR
7CDF	LR	ND	ND	ND	0.06^{1}	ND	ND	ND	LR
8CDF	LR	4.1	0.1	ND	0.3	ND	ND	0.5	LR
total CDD	-	26	3.0	7.3	11	1.2	2.8	63	-
total CDF	-	52	2.8	1.7	25	19	ND	68	-
total CP	ND	5.1	20	ND	6.0	ND	ND	28	ND
total CB	6.1	58	9,200	6.3	260	8,500	4.6	2,200	6,200
total PCB	5.8	15	17	39	89	67	8.5	230	8.3

* 24-hour sampling times; sampling volumes were - Test 1, 15.60 m³; Test 2, 15.82 m³; Test 3, 15.73 m³. Superscripts are number of isomers observed.

All CDD/CDF values corrected for recovery. Average percent recoveries, including rejected samples, were: filter, 17±16; impinger, 160±150; florisil, 99±89.

The concentrations of PCDDs and PCDFs in the raw sludge and bottom ash samples are listed in Table LXII. The hepta- and octachlorinated PCDDs and PCDFs were the only isomers which were detected in the sewage sludge. In an earlier study, these isomers were found to be the dominant PCDD and PCDF species in the analysis of municipal refuse (Tosine et al., 1985). Similarly, the total amount of PCDDs in the raw refuse was found to be higher than the total amount of PCDFs. Chlorinated benzenes, found in relatively large levels in the stack gases, were present at levels slightly less than the PCDDs in the raw sludge. The bottom ash samples which were analyzed were found to contain virtually no chlorinated organic compounds.

Reproduced from best available copy.

Table LXII: Concentrations of Chlorinated Organics in Raw Sludge and Bottom Ash
All data are [ng/g dry sample weight]

	RAW SLUDGE			BOTTOM ASH		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
4CDD	ND	ND	ND	ND	ND	ND
5CDD	ND	ND	ND	ND	ND	ND
6CDD	ND	ND	ND	ND	ND	ND
7CDD	79	70	110	ND	ND	0.4
8CDD	230	150	140	ND	ND	0.8
4CDF	ND	ND	ND	ND	ND	ND
5CDF	ND	ND	ND	ND	ND	ND
6CDF	ND	ND	ND	ND	ND	ND
7CDF	21	12	12	ND	ND	ND
8CDF	25	18	9	ND	ND	ND
^{13}C1-8CDD % recovery	53	33	33	19	25	14
total CDD	310	220	250	ND	ND	1.2
total CDF	46	30	21	ND	ND	ND
total CP	<1	ND	ND	ND	ND	ND
total CB	190	77	130	5	1	2
total PCB	4	2	1	5	21	4

ND: not detected, CDD/CDF single congener average detection limits ranged from 0.1 to 0.5 ng/g (tetra to octa congeners) for Bottom ash samples, and 1 to 3 ng/g (tetra to octa) for raw sludge samples.

IV. HAZARDOUS WASTE INCINERATION

The performance of a high-temperature incinerator used for the destruction of chlorine-containing industrial wastes was evaluated with respect to its emission of dioxins (Brenner et al., 1984). The incinerator consisted of a rotating slag tap furnace, a secondary combustion chamber, a waste heat recovery boiler, and scrubbing units. Both liquid and solid industrial wastes could be delivered to the furnace. Two burners located in the front wall were used to keep the kiln temperature at about 1,000 °C or higher. Flue gases leave the kiln and enter a refractory-lined secondary combustion chamber where combustion is completed. The temperature is kept between 900 and 1,400 °C by the combustion of sufficient quantities of liquid waste using compressed-air atomizer burners. The flue gases are then cooled to 250 °C in the waste heat boiler and finally to about 50-70 °C after passage through two scrubber stages. Acid gases are scrubbed with a sodium hydroxide solution. The emissions of the plant were monitored at the stack as well as in the wash water circuit.

The operating conditions and wastes combusted in the experiments performed are summarized in Tables LXIII and LXIV. In experiment 2b, chlorine-free waste used in the blank run was incinerated along with the chlorine-containing waste thereby reducing the chlorine feed rate in comparison to experiment 1. In all of the experiments, no PCDDs were detected (detection limits ranged from 1 to 6 ng/Nm^3 for the different homologues). It must be noted that the recoveries based on ^{13}C-labelled 2,3,7,8-Cl_4DD sample spikes were quite varied and low. The workers claimed that operation of the rotary kiln at 1,000 °C and residence times of 3 to 7 seconds resulted in dioxin-free emission, however it is more likely that the PCDDs were present but below the detection limit of the analytical methodology employed.

Table LIII: Technical Parameters during Experiments 1, and 2

	Kiln Temperature [°C]	Residence[1] Time of Gases	Throughout [kg/h]	% Cl	Wash Water Circuit [m^3/h]	Stack Gases		
						HCl [mg/Nm^3]	CO [mg/Nm^3]	O_2
Exp.1	about 1,000	3-7 sec	2,800	9	200	8	5	14.5
Exp.2a	about 1,000	7 sec	2,860[2]	0	200	0	8	14.5
		7 sec	1,700[3]	0				
Exp.2b	about 1,000	3 sec	1,100[3]	9	200	5	5	14.5

[1] 2 burners in kiln (7 sec), 2 burners in secondary combustion Chamber (3 sec)

[2] blank experiment, chlorine-free waste

[3] waste from experiment 2a was burned in the kiln during incineration of the chlorine-contain waste in the secondary combustion chamber.

Table LIV: Incinerated Wastes

	C %	C %	Type of Waste
Exp. 1	60	9	Distillation sump from chlorinated phenols and cresols
Exp. 2a	53	0	Mixture of alcohols and aldehydes with a boiling point > 150 °C
Exp. 2b	60	9	Distillation sump from chlorinated phenols and cresols

Brenner et al. studied the emission of PCDDs resulting from the high-temperature incineration of chlorine-containing industrial wastes (Brenner et al., 1986). Table LXV lists the types of chlorine-containing wastes which were incinerated in the experiments. It should be noted that additional chlorine-free waste was added to the kiln to keep the burning temperature of the kiln and secondary combustion chamber between 1,130-1,230 °C (see Table LXV). In all four experiments, natural gas was also fed into the system to help regulate the temperatures. Table LXVI gives the waste characteristics for the incineration experiments. PCBs and chlorinated benzenes were fed into the kiln via burners specifically designed for handling viscous wastes.

Table LXV: Technical Parameters during PCB-Burning Experiments

** burners in kiln (7 sec), secondary combustion chamber (3 sec)

+ burners 1,2,5 are compressed-air atomizer burners; burners 1a and 2a serve for dosage of pasty and viscous material (e.g. PCBs)

	kiln temp. °C	residence time of gases sec	PCB-throughput t/h	fire feed t/h	sustain no of burners in action +)	PCB %	chlorine %	stack gases O_2, Vol-%
Exp. 1	1180/1230*	3 - 7 **)	1.04	3.01	1, 2, 5 & 1a	100	about 56	7 - 12
Exp. 2	1170/1220	3 - 7 **)	0.74	2.65	2, 5, 1a & 2a (for pasty material)	100	about 56	9.5 - 10.5
Exp. 3	1140/1230	3 - 7 **)	"0.72"	3.26	1, 2, 5, 1a & 2a	poly chloro-benzene sump	about 65	10 - 12
Exp. 4	1130/1220	3 - 7 **)	0.97	3.55	1, 2, 5, 1a & 2a	100	about 56	9 - 10.2

Table LXVI: Incinerated Wastes, Additional Wastes for Fire Sustain

* drums C contained polychlorobenzene sumps

	waste	PCB %	Cl % *	type of wastes for fire sustain	remarks
Exp. 1	container A	100	about 56	distillation sump, chlorine-free, C, H, O-compounds	PCB's always fed through burner 1a for pasty material; during exp. 2 to 4 burner 2a additionally served for dosage of fire sustain material; during all four experiments natural gas was fed in order to keep the preset temperatures
Exp. 2	container B	100	about 56	similar to exp. 1	
Exp. 3	drums C	- *)	about 65 *)	similar to exp. 1	
Exp. 4	container D	100	about 56	distillation head and sump C, H, O, N-compounds, chlorine-free	

The flue gas emissions , the slags, and the wash water were all analyzed for their PCDD content. In experiment 1 and 3 the stack emissions were analyzed and in experiments 2 and 4 the unscrubbed flue gas leaving the waste heat boiler was analyzed. The gaseous emissions were sampled using impingers and the polyurethane foam plug method. The results of the experiments are summarized in Table LXVII (Brenner et al., 1986).

Table LXVII: Analytical Results for Experiment 1 to 4;
Values for Emission in [ng/g], for Slags and Wash Water in ppt [ng/kg]

	recovery ^{13}C-2,3,7,8-TCDD %	-Di Σ	-Tri Σ	2,3,7,8-TCDD	Tetra Σ	Penta Σ	Hexa Σ	Hepta Σ	Octa
Exp. 1									
1.1. Stack emission									
1.1.1. Impinger sampling *									
Water separator + probe	51	<0.1	<0.1	< 0.1**	<0.1	<0.1	<0.1	<0.1	0.4*
Impinger 1 & 2	75	<0.1	<0.1	< 0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1.1.2. PFP-technique									
Water separator + probe	54	<0.1	<0.1	< 0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PU-foam plugs	100	1.3	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
1.2. Slag	10	<50	<50	<5	<5	<50	<50	<50	<50
1.3. Wash water	79	<5	<5	<1	<1	<5	<5	<5	<5

Table LXVII: Analytical Results for Experiment 1 to 4; Continued

Exp. 2									
2.1. Crude exhaust									
2.1.1. Impinger sampling									
Water separator + probe	34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Impinger 1 & 2	90	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
2.1.2. PFP-technique									
Water separator + probe	46	4	3	<0.1	0.5	<0.1	<0.1	<0.1	<0.1
PU-foam plugs	114	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2.2. Slag	7	<10	<10	<10	<10	<10	<10	<10	<10
2.3. Wash water	116	<5	<5	<1	<1	<5	<5	<5	<5
Exp. 3									
3.1. Stack emission									
3.1.1. Impinger sampling									
Water separator + probe	58	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Impinger 1 & 2	80	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3.1.2. PFP-technique									
Water separator + probe	130	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PU-foam-plugs	13+	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3.2. Slag	21	-**	-**	<10	<10	<10	<10	<10	<10
3.3. Wash water	110	-**	-**	<1	<1	<5	<5	<5	<5
Exp. 4									
4.1. Crude exhaust									
4.1.1. Impinger sampling									
Water separator + probe	88	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0
Impinger 1 & 2	93	1.8	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
4.1.2. PFP-technique									
Water separator + probe	95	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	10	20
PU-foam plugs	74	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	5.0
4.2. Slag	4	<50	<50	<30	<30	<50	<50	<50	<50
4.3. Wash water	50	-	-	<1	<1	<1	<1	<1	<1

+ low recovery due to experimental difficulties

++ not determined because of noisy signals

* values given below 1 ng/m³ or 1 ppt indicate trends, for reproducibility, determination and detection limits see text

** the sign indicates "not detected" - detection limit given

Reproduced from best available copy.

For all experiments, only trace amounts of PCDDs, usually near the detection limit, were found in the flue gases analyzed. The polyurethane foam plug method was found to be as effective as the impinger technique for trapping trace amounts of PCDDs. The analyses of the slags and wash water samples revealed no detectable levels of PCDDs.

The incinerator was found to effectively destroy PCBs and chlorinated benzenes without producing significant levels of PCDDs (below limits usually observed for many incinerators). The good performance of this incinerator was attributed to:

1. Effective spraying and subsequent mixing of the waste with air
2. Two-step burning of the waste thereby creating an afterburner effect
3. Long residence times in the kiln and secondary combustion chamber (7 and 3 seconds respectively)
4. High temperatures in the kiln and secondary combustion chamber
5. Long residence time of the slag at the melt temperature

The use of PCBs was banned in Japan in 1972, at which time more than 5,000 tons were confiscated and placed in storage tanks (Tsuji et ai., 1987). The incineration of liquid PCB waste was studied in a series of tests in 1985. The PCB waste incinerator, capable of burning 210 kg/h, is shown in Figure 33. The residence time in the combustion chamber, which is maintained at 1,400 °C, is 2 seconds. Flue gases are passed through a treatment system consisting of a water scrubber, for gas cooling and elimination of HCl, and activated carbon beds for the removal of trace levels of hazardous by-products. The used water is passed through activated carbon and stored in a checking tank so that levels of PCDDs, PCDFs, and PCBs in the water could be determined. If the water in the tank contained levels higher than permissible, the water was recycled through the activated carbon beds. After neutralization, waste water is discharged into a lake.

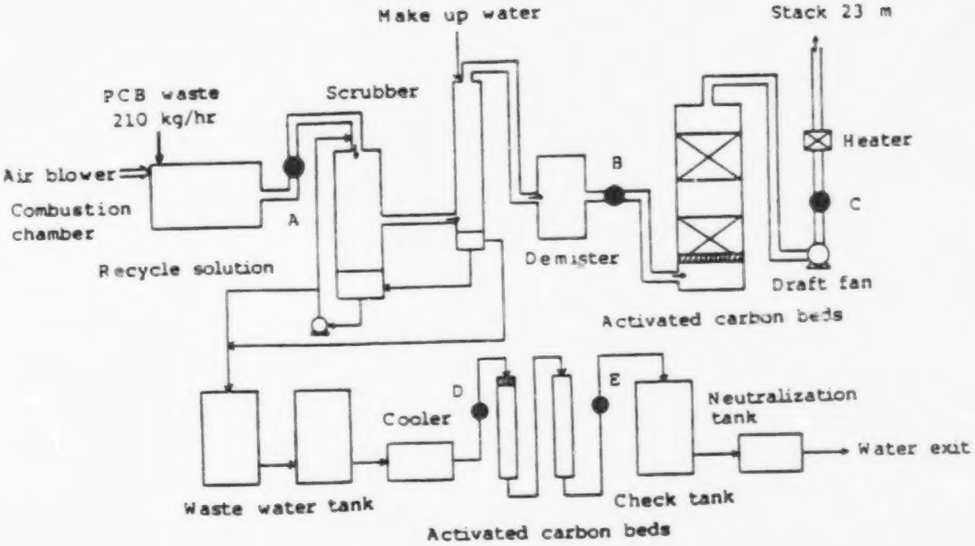


Figure 33: Flow Diagram of Liquid PCB Waste Incineration System

● Monitoring point for gas and water

▨ Samples for combustion products analysis

During the test period, concentrations of PCDDs, PCDFs, and PCBs in the stack emissions and waste water exiting the plant were monitored. The levels of PCBs were found to be less than the maximum permissible levels of 0.05 $\mu g/Nm^3$ in air and 0.05 $\mu g/L$ in water. The efficiency of decomposition and removal of PCBs was calculated to be greater than 99.99999%. The levels of PCDDs and PCDFs in the incinerator emissions were also lower than the maximum permissible levels of 0.1 ng/Nm^3 in air and 0.003 ng/L in water.

Undecomposed materials were accumulated on the activated carbon beds which were analyzed for their content of PCDDs, PCDFs, and PCBs. The results of these analyses are shown in Figure 34.

The levels of PCDDs and PCDFs in combustion effluents from hazardous waste incinerators reported in various studies are summarized in Table LXVIII (Ontario Minstry of the Environment, (1985). It is interesting to note that the levels in the earlier reports are higher than those in the later studies which suggests that technological advances have been made in reducing emissions from hazardous waste incinerators.

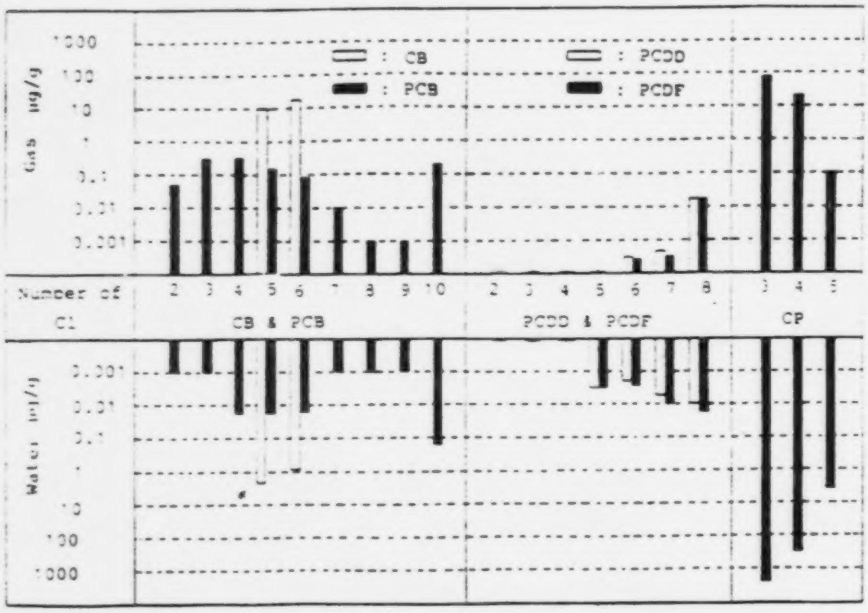


Figure 34: Levels of Combustion Products Found in Activated Carbon

Table LXVIII: PCDD and PCDF Concentrations in Combustion Effluents from Industrial Chemical Waste Incineration

REFERENCE	MATERIAL COMBUSTED	SOURCE/ DESCRIPTION	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
Buser & Bosshardt (1978)	Used industrial oils	Industrial Heating Facility - Switzerland	Fly ash (ng/g)	100	160	180	130	40					
Dow Chemical Co. (1978)	Tars & natural gas	Waste Incinerators - Midland, Mich., USA Stationary Tar Burner	Stack Collected Particulate-Ave (ng/g)	2,3,7,8- ND Other Isomers ND		8	92	300					
	Tars, Solid Waste & Natural Gas	Rotary Kiln (without supplementary fuel)	Stack Collected Particulates Ave. (ng/g)	2,800 5,500		21,000	16,000	263,000					
	Tars, solid waste, natural gas	Rotary Kiln (with supplemental fuel)	Stack Collected Particulate Ave. (ng/g)	2,3,7,8- ND Other Isomers ND		2.0	32.0	230.0					
Hryhorczuk (1981)	Electrical wires, cable, x-ray films	Wire Reclamation Incinerator - Illinois, USA	Ash from base of stack (ng/g)	58					730				
			Ash from top of stack (ng/g)	410					11,600				

Reproduced from best available copy.

Table LXVIII Continued: PCDD and PCDF Concentrations in Combustion Effluents from Industrial Chemical Waste Incineration

REFERENCE	MATERIAL COMBUSTED	SOURCE/ DESCRIPTION	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
Tiernan et al. (1982b)	Test 1 Liquid chlorinated hydrocarbon wastes (vinylchloride, still bottoms)	Rollins Environmental Services - Deer Park Texas, USA rotary kiln and liquid injection burner feeding common afterburner.	Total sampling train (ng/ sample)	6.94					13.5 (1.5)**				
	Test 2 Per Test 1, plus liquid PCB waste	Per Test 1	Total of all parts of sampling train (ng/sample)	1.42			*		22.0 (2.45)**				
	Test 3 Liquid PCB wastes and clean fuel oil	Per Test 1	Total sampling train (ng/ sample)	0					2.0 (0.2)**				
	Test 1 shredded capacitors (solid - no PCB) plus chlorinated hydrocarbons (pesticide process and paint/ink manufacturing waste)	Energy Systems Co. - El Dorado, Arkansas, USA rotary kiln and afterburner with 2 combustion chambers -	Total sampling train (ng/ sample)	0.263					2.0 (0.5)**				

* - 2,3,7,8-T_4CDD
** - 2,3,7,8-T_4CDF

Table LXVIII Continued: PCDD and PCDF Concentrations in Combustion Effluents from Industrial Chemical Waste Incineration

REFERENCE	MATERIAL COMBUSTED	SOURCE/ DESCRIPTION	SAMPLE MATRIX (UNITS)	PCDD *					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
Tiernan *et al.* (1982b) (Cont'd)	Test 2 Per Test 1, plus liquid PCBs and shredded PCB containing capacitors	Per Test 1	Total sampling train (ng/ sample)	0.476 0.476					6.0 (1.5)**				
	Test 3 Liquid PBC wastes and PCB containing capacitors mixed with diesel fuel	Per Test 1	Total sampling train (ng/ sample)	0					0 (0)**				
Chiu *et al.* (1983)	Aroclor 1254 (PCB) mixed with methanol	Experimental Plasma Reactor - Canada Feb., 1982	Stack gas (ng/dscm)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Leung and Meadows (1984)	Askarel (20% by-weight Aroclor 1260)	June, 1983	Stack gas (ng/dscm)	ND	ND	ND	ND	ND	ND	2500	400	10	ND

* - 2,3,7,8-T_4CDD
** - 2,3,7,8-T_4CDF

Table LXVIII Continued: PCDD and PCDF Concentrations in Combustion Effluents from Industrial Chemical Waste Incineration

REFERENCE	MATERIAL COMBUSTED	SOURCE/ DESCRIPTION	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
ppe *et al.* (1983a)	pentachlorophenol	Industrial Boiler - USA	Baghouse ash (ng/g)	960 (<5)*	1,400	2,000	700	200	900 (100)**	1,500	150	60	6
			Bottom ash (ng/g)	10 (<1)*	20	40	100	140	ND (ND)**	ND	ND	ND	-
	PCB (Oil-fired)	Rotary cement kiln - Slemmestad, Norway	Electrostatic filter (ng/g)	<1.0	<1.5	<2.5	<0.3	<0.5	<1.0	<2.5	<2.5	<5.0	<0.5
			Stack Gas Condensate (ng/L)	<0.2	<0.1	<0.6	<0.2	<0.4	<0.2	<0.04	<2.4	<4.6	<1.0
			XAD Filter 1 (ng/g)	<0.1	<0.05	<0.7	<0.1	<0.2	<0.1	<0.05	<0.7	<1.4	<0.3
			XAD Filter 2 (ng/g)	<0.05	<0.05	<0.2	<0.05	<0.1	<0.2	<0.05	<0.3	<3.0	<0.3
			Filter 1 (ng)	<3.0	<6.3	<6.3	<0.3	<0.6	<6.3	<6.3	<6.3	<6.3	<1.3
			Filter 2 (ng)	<0.1	<0.2	<0.9	<0.1	<0.4	<0.1	<0.2	<0.9	<0.2	<0.4
			Sintered cement (ng/g)	<50.0	<50.0	<250.0	<5.0	<250.0	<50.0	<50.0	<250.0	<50.0	<250.0
oss *et al.* 1983)	PCBs 20% chlorobenzenes, kerosene, pump oils, sulphur (250 ppm) (total 350 tonnes burned)	M/T Vulcanus Incinerator Ship - Gulf of Mexico, USA	Stack gas (excludes partic.) (ng/m^3)	ND					<0.3-<3.0				

- 2,3,7,8-T_4CDD
- 2,3,7,8-T_4CDF

duced from
ailable copy.

f

V. TRANSFORMER AND CAPACITOR FIRES

PCDFs have been synthesized by pyrolyzing individual PCB isomers (Hileman et al., 1985). Additional PCDFs were created by chlorination or dechlorination of individual PCDFs to produce at total of 110 different isomers. Chlorination was accomplished using antimony pentachloride while ultraviolet (UV) photolysis was employed for dechlorination purposes.

At elevated temperatures, such as those in transformer fires, PCBs can undergo reactions to PCDFs and other by-products (Erickson et al., 1985). A study was therefore undertaken to determine the optimal conditions for PCDF formation and to study the potential for formation of PCDFs and PCDDs from the combustion of selected PCB-containing dielectric fluids.

Experiments were conducted using a bench-scale thermal destruction unit to determine the effects of temperature, oxygen, and residence time on the formation of PCDFs. A mineral oil was spiked with three PCB isomers which form PCDFs via known reaction mechanisms. Based on the results obtained from 33 test runs, it was concluded that both temperature and oxygen levels have significant effects on PCDF formation. From this study, the optimal conditions were determined to be a temperature of 675 °C with an excess oxygen concentration of 8%. The residence time did not play as important a role in the range from 0.3 to 1.5 seconds, although slightly lower yields appeared to occur at the shorter residence times.

Duplicate test runs were then performed using mineral oil and silicone oil dielectric fluids containing Aroclor 1254 at concentrations of 0, 5, 50, and 500 ppm. All runs were carried out using the pre-determined optimal conditions (a residence time of 0.8 second was used for all tests). PCDFs were found in all of the combustion test runs except for the blanks (0 ppm Aroclor 1254). The results for the mineral oil runs are illustrated in Figure 35. No discussion is given by the researchers regarding why some of the points on the plot represent averages of two values while others are from single determinations. Therefore the reproducibility of the results for the levels of the various PCDF homologues formed are somewhat questionable.

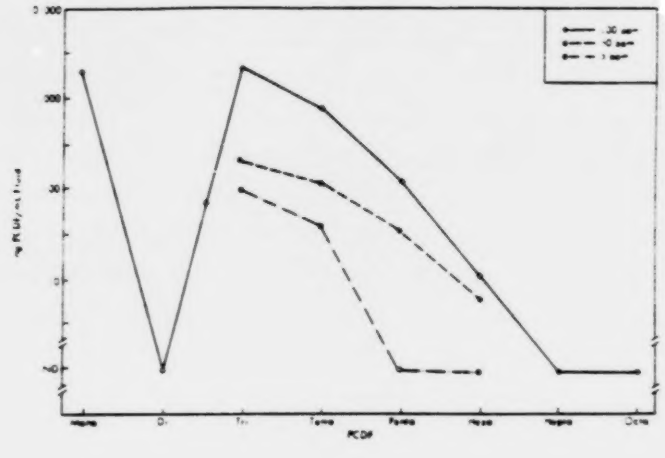


Figure 35: PCDF Formation in Mineral Oil by Homolog
Closed symbols are averages of two values; open symbols are single determinations

The total amounts of PCDFs formed for the incineration of the mineral and silicone oils containing various levels of PCBs are shown in Figure 36. An approximate linear relationship could be observed for the results for both types of dielectric fluid. PCDDs were reported found at low levels in some of the samples, however, these may be due to artifacts.

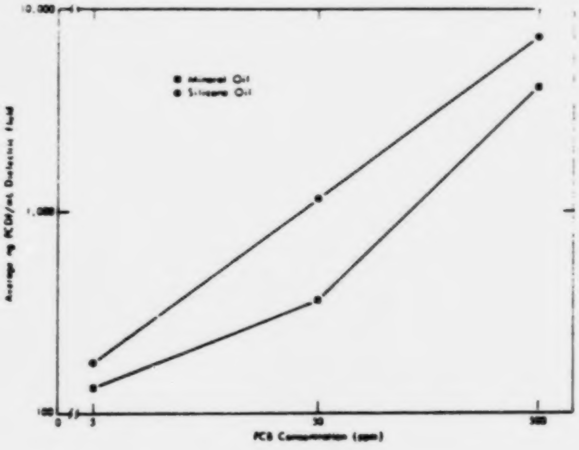


Figure 36: Average PCDF Formation Versus PCB Concentration

Reproduced from
available copy.

A PCB-containing askarel (70% Aroclor 1260) and a non-PCB askarel (consisting of mainly trichlorobenzenes with some tetrachloro-benzenes present) were tested in duplicate under the same conditions used for the mineral and silicone oils. PCDFs were produced in all of the runs, the results of which are given in Figure 37. Interestingly all eight PCDF homologues were detected in the PCB-askarel tests. with a crude bell-shaped distribution being centered about the Cl_5DFs. PCDDs were found to be produced from the chlorobenzene askarel, however at levels much lower than the PCDFs. It must be remembered that the conditions used were based on those optimized for PCDF formation and therefore perhaps more PCDDs would be produced under different conditions.

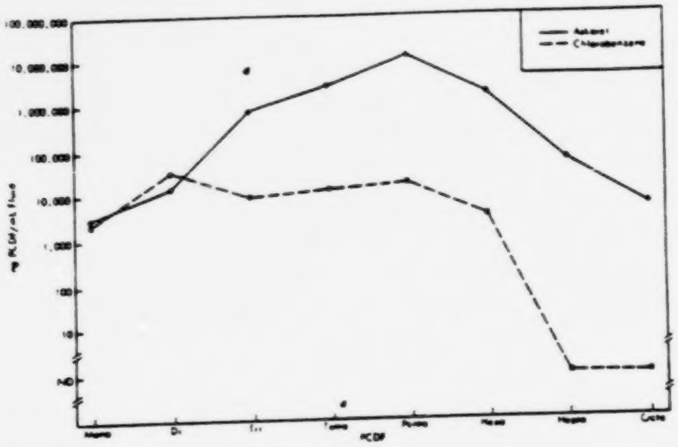


Figure 37: PCDF Formation from PCB Askarel and Trichlorobenzene Fluid
Closed symbols are averages of two values; open symbols are single determinations

A conversion efficiency of up to 4% PCB-to-PCDF was observed for the mineral oil and silicone oil tests. The PCB-askarel fluid gave a conversion efficiency of 3%, which is quite similar to that observed for the other dielectric fluids. Conversion efficiency for the chlorobenzene askarel was much lower, 0.004% PCB-to-PCDF, than for any of the PCB-containing fluids. The conversion of tri- and tetrachlorobenzenes to PCDDs was even less efficient, giving a yield of only 0.0001%.

The results of the study are summarized in Tables LIX and LX (des Rosiers and Lee, 1986).

Table LIX: PCDDs Formed in Combustion Studies I

RUNS	MonoCDF (ng)	DiCDF (ng)	TriCDF (ng)	TetraCDF (ng)	PentaCDF (ng)	HexaCDF (ng)	HeptaCDF (ng)	OctaCDF (ng)	PCDFs (ng)
Mineral Oil/	-[a]	-	130	49	NQ[b]	0[c]	-	-	180
5 ppm A-1254	-	-	43	23	0	0	-	-	66
Silicone Oil/	-	-	25	0	90	0	-	-	115
5 ppm A-1254	-	-	31	9	150	0	-	-	190
Mineral Oil/	-	-	200	110	39	8.5	-	-	350
50 ppm A-1254	-	-	140	82	21	2.2	-	-	250
Silicone Oil/	-	-	290	73	62	0	0	0	420
50 ppm A-1254	-	-	530	640	83	0	0	0	1,300
Mineral Oil/	1,700	0	2,200	690	43	7	0	0	1,700
500 ppm A-1254	-	-	1,300	620	170	13	0	0	2,100
(B)	-	-	0	13	0	0	0	0	13
Silicone Oil/	-	-	2,000	740	340	45	-	-	3,100
500 ppm A-1254	50	1,300	5,000	2,100	170	12	0	0	8,600
(B)	0.4	0	0	0	0	0	0	0	0
70% A-1254/30%	810	5,100	440,000	1,400,000	6,400,000	910,000	29,000	3,400	9,200,000
Trichlorobenzene	1,900	7,000	220,000	1,100,000	4,700,000	660,000	19,000	1,300	6,700,000
(B)	28	190	310	1,200	17,000	3,000	-	-	22,000
Chlorobenzene Fluid	-	-	2,400	2,600	5,000	0	-	-	9,300
(tri with some tetra)	2,000	29,000	>13,000	>19,000	>22,000	5,200	0	0	>90,000
(B)	-	-	81	25	5	0	-	-	110
Lab Blank	0	0	0	0	0	0	-	-	0

[a] - = not analyzed.
[b] NQ = not quantitated.
[c] 0 = not detected.

Table LX: PCDDs Formed in Combustion Studies II

Runs	MonoCDD (ng)	DiCDD (ng)	TriCDD (ng)	TetraCDD (ng)	PentaCDD (ng)	HexaCDD (ng)	HeptaCDD (ng)	OctaCDD (ng)	PCDDs (ng)
Silicone Oil/	-	-	0	0	7.7	0	-	-	7.7
500 ppm Aroclor 1254	0	0	0	0	1.7	0	0	0	1.7
70% Aroclor 1254/	0	0	0	0	0	0	330	37	360
30% Trichlorobenzene	0	0	0	0	0	0	230	51	290
Chlorobenzene Fluids	-	-	1,100	440	0	0	-	-	1,500
(mostly tri with some tetra)	0	0	630	520	0	72	0	0	1,200

Reproduced from
best available copy.

Erickson et al. studied the formation of by-products from the thermal degradation of dielectric fluids including those contaminated by PCBs (Erickson et al., 1986). A bench-scale thermal destruction unit, shown in Figure 41, was used to combust the samples. In this system, the dielectric fluid is fed continuously with a syringe pump. The effluent from the combustion furnace is passed through an XAD-2 trap where the volatilized organics are collected. The extracts were then analyzed by HRGC/EIMS in the selected ion monitoring mode for their PCDD and PCDF contents.

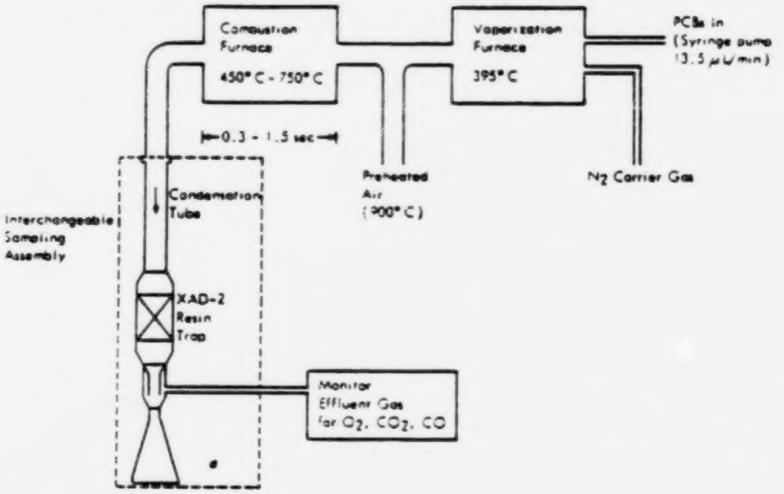


Figure 38: Thermal Combustion System to Model PCB Fire Conditions (Temperature, pressure, and flow rates are monitored throughout the system)

Reproduced from best available copy.

In previous work, the optimum conditions for PCDF formation from the thermal degradation of PCBs were found to be at a temperature of 675 °C for a residence time of 0.8 seconds (or longer), with an excess of 8% oxygen (Erickson et al., 1985). Using these conditions, PCDF and PCDD formation was investigated for the combustion of PCB, trichlorobenzene, and tetrachloroethylene transformer dielectric fluids. The results, including averages and variations of conversion efficiencies, are shown in Figure 39. The highest PCDF formation clearly arises for the thermal destruction of PCB feed and the least efficient production is observed for the tetrachloroethylene feed. In all runs, the amount of PCDDs formed were much lower than the amount of PCDFs formed for the same feed material. The most efficient conversion of dielectric fluid to PCDDs was observed for the trichlorobenzene feed while the tetrachloroethylene feed again resulted in the lowest conversion efficiency. It should be noted, however, that the combustion conditions used in all of the runs were based on the optimum conditions for the formation of PCDF from PCB-containing dielectric fluids. Therefore these results do not imply that they represent the maximum conversion yields since the optimum conditions for the other fluids may be quite different. Similarly, the formation of PCDDs were studied under optimum conditions for the formation of PCDFs from PCBs.

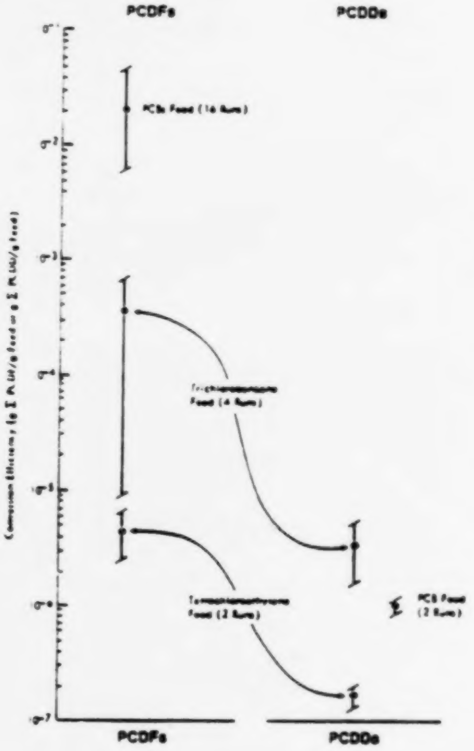


Figure 39: Comparison of PCDD and PCDF Formation from PCB, Trichlorobenzene, and Tetrachloroethylene Feeds

Figures 40-42 show the distributions of the PCDF and PCDD homologues formed from the thermal degradation of the three dielectric fluids studied.

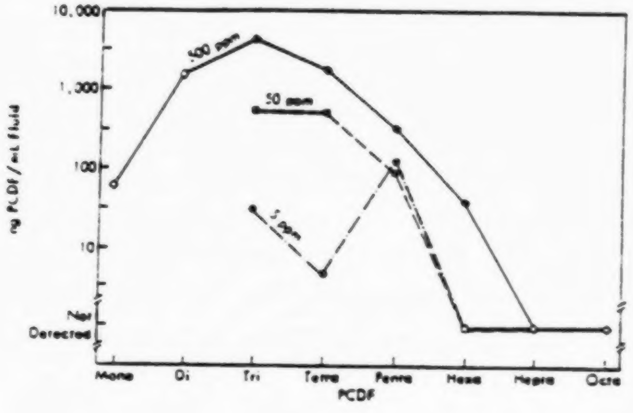


Figure 40: PCDF Formation from Aroclor 1254 in Silicone Oil by Homolog
Closed symbols are averages of two values;
Open symbols are single determinations;
Missing points are no data.

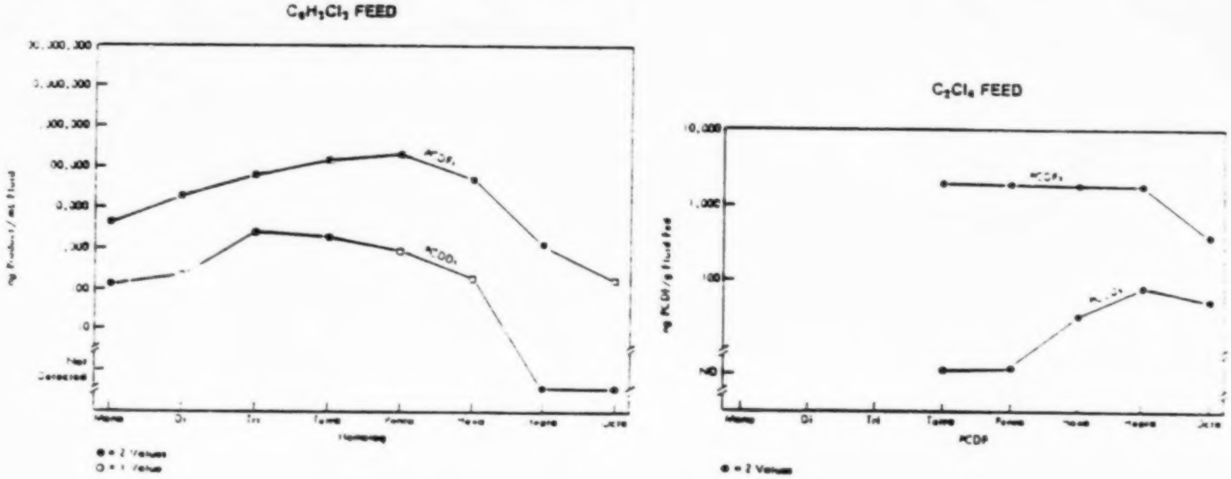


Figure 41: PCDF Formation from Trichlorobenzene Feed (left) and Tetrachloroethylene Feed (right)
(Symbols same as above)

Reproduced from best available copy.

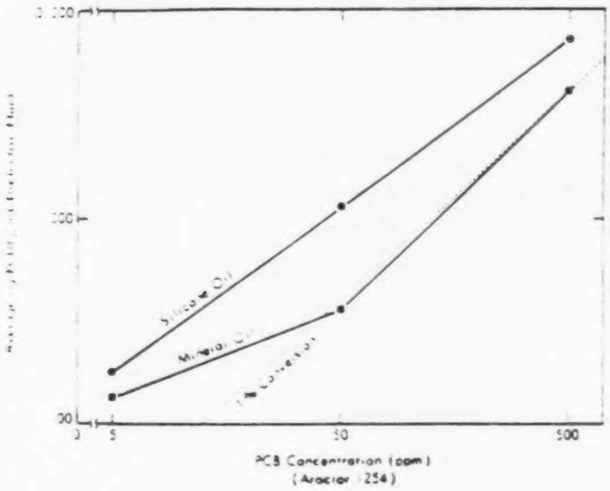


Figure 42: Average PCDF Formation Versus PCB Concentration (675 °C for 8 s with 8 % excess oxygen)

The major user of PCBs has been the electric utility industry (Addis, 1986). The occurrence of several PCB fires and the link between such thermal processes and the formation of toxic by-products, specifically PCDFs, have resulted in efforts to eliminate PCBs in transformers. This can be accomplished by either retrofilling or complete replacement of the transformer. The former method is not easily accomplished since it is very difficult to remove all traces of PCBs and the transformer must be reclassified as uncontaminated (below 50 ppm PCB) before it can be used. Even with present technology, removal of residual PCBs is not convenient and therefore complete replacement of the transformer is often carried out. Disposal of a transformer requires draining of the PCB and subsequent flushing with solvent. The liquids must then be destroyed in an authorized incinerator and the transformer itself is sent to a certified landfill.

A further problem is the roughly 2 million mineral oil transformers which have been inadvertantly contaminated with PCBs over the years. While most of these are contaminated at about the 50 ppm level, 10% are contaminated at the 500 ppm level and therefore must be treated as PCB transformers.

Studies are therefore necessary to investigate the resulting by-products from the thermal degradation of PCBs, whether they are in their concentrated state or present as contaminants in mineral and silicone oils. Tetrachloroethylene has been proposed as a replacement fluid and PCB contamination of this material is also of interest.

In a study of pyrolysis (high temperature decomposition in an oxygen-depleted atmosphere) and combustion (oxidation in the presence of an open flame and an excess of air), Aroclor 1254, in both its "neat" form and as a contaminant in mineral oil, silicone and tetrachloroethylene, was subjected to thermal degradation (Addis, 1986).

The conversion of PCBs to PCDFs was found to reach a maximum at a temperature of approximately 550 °C in the pyrolysis experiments and was therefore the temperature used (unless otherwise indicated in the Tables). All runs were conducted for a 15 minute time period. A series of six runs were made for every set of conditions, all within the same day. The six runs were randomly combined prior to cleanup to yield two composite samples for analysis. Tables LXI and LXII show the resulting levels of PCDF which were formed in the the pyrolysis experiments (Table LXI shows the results in ng/g of total mixture pyrolyzed whereas Table LXII shows the results in ng/g of Aroclor 1254).

Table LXI: PCDF Formed [ng/g] of "Mixture pyrolyzed: Aroclor 1254 in Insulating Fluids"

Sample	Description	2378[2] TCDF	Total TCDF	12378[2] PeCDF	Base Peak PeCDF	Total PeCDF	Base Peak HxCDF	Total HxCDF	Total HeCDF	OCDF
42582	100% Aroclor 1254	1,300	8,200	-	-	16,000	8,000	8,000	60	-
42583	100% Aroclor 1254	965	5,500	-	-	10,000	5,100	5,100	-	-
50854	5,000 ppm[1] in mineral oil	15.0	45.0	17.0	62.0	165	87.0	162	24.0	< 2
50855	5,000 ppm in mineral oil	11.8	33.0	17.2	55.0	171	60.0	205	14.0	0.23
50856	500 ppm in mineral oil	1.6	-	1.8	6.7	17.2	6.3	16.8	< 10	-
50857	500 ppm in mineral oil	1.1	3.1	1.9	5.8	18.2	6.8	18.1	2.2	-
50858	50 ppm in mineral oil	-	-	0.4	1.1	3.1	1.5	3.5	-	-
50859	50 ppm in mineral oil	-	-	0.9	1.7	3.4	1.3	-	-	-
45298	5,000 ppm[3,4] in silicone	9.9	107.0	4.5	-	70.0	2.2	6.9	0.15	-
44295	5,000 ppm[5] in tetrachloroethylene	1.2	2.9	4.6	-	28.0	5.5	12.5	0.9	-
42571	Native mix[6] in mineral oil									
	Added	9.3	-	17.2 (23478)	-	32.4 (234 78)				
	Found	9.1	-	17.5	-	23.0			47	56 (OCDD)

(1) Each mineral oil sample represents a composite of three separate pyrolyses which were combined prior to analysis to minimize run-to-run variation. All pyrolyses at 550°C for 15 minutes.
(2) Includes coeluters on DB-5 column.
(3) 650°C.
(4) Chlorinated fluorenes(?) at 10x higher level.
(5) 600°C.
(6) Mineral oil spiked with PCDFs to test method.

Table LXII: PCDF Formed [ng] per Gram of Aroclor 1254 Pyrolyzed in Insulating Fluid

Sample	Description	2378[2] TCDF	Total TCDF	12378[2] PeCDF	Base Peak PeCDF	Total PeCDF	Base Peak HxCDF	Total HxCDF	Total HeCDF	OCDF
42582	100% Aroclor 1254	1,300	8,200	-	-	16,000	8,000	8,000	60	-
42583	100% Aroclor 1254	965	5,500	-	-	10,000	5,100	5,100	-	-
50854	5,000 ppm[1] in mineral oil	3,000	9,000	3,400	12,400	33,000	17,400	32,400	4,800	64
50855	5,000 ppm in mineral oil	2,360	6,600	3,440	11,000	34,200	12,000	41,000	2,800	46
50856	500 ppm in mineral oil	3,200	-	3,600	13,400	34,400	12,600	33,600	-	-
50857	500 ppm in mineral oil	2,200	6,200	3,800	11,600	36,400	13,600	36,200	4,400	-
50858	50 ppm in mineral oil	-	-	8,000	22,000	62,000	30,000	70,000	-	-
50859	50 ppm in mineral oil	-	-	18,000	34,000	68,000	26,000	-	-	-
45298	5,000 ppm[3] in silicone	1,960	21,400	900	-	14,000	440	1,380	30	-
44295	5,000 ppm[4] in tetrachloroethylene	240	580	960	-	5,600	1,100	2,500	180	-

(1) Each mineral oil sample represents a composite of three separate pyrolyses. These were combined prior to analysis to minimize run-to-run variation. All pyrolyses at 550°C for 15 minutes.
(2) Includes coeluters on DB-5 column.
(3) 650°C.
(4) 600°C.

The combustion of PCB-contaminated dielectric fluids was also studied. The results of these studies are given in Table LXIII. The conversion for the tri- to heptachlorodibenzofuran isomer groups was found to be near optimum for a combustion wall temperature of 550 °C and a residence time of 3 seconds. Mineral oil contaminated with PCB levels of 5000, 500, and 50 ppm produced similar levels of tri-, tetra-, and pentachlorinated furans (relative to the amount of PCBs present) and in all cases no Cl_6DFs or Cl_7DFs were detected. The PCB-contaminated tetrachloroethylene mixtures all produced higher yields of the more chlorinated PCDF isomers than observed for the mineral oil tests. Also interesting to note was the fact that in both the pyrolysis and combustion of tetrachloroethylene contaminated with Aroclor 1254, different Cl_4DF- and Cl_5DF isomers were produced than for either the "neat" Aroclor or the contaminated mineral oil.

It must be stressed that these results cannot be used to explain results of accidental PCB fires since the conditions for such occurrences are completely random. However, these results do imply that the by-products of PCB fires will most likely include PCDFs.

Table LXIII: Combustion of Aroclor 1254 in Insulating Fluids at 550 °C - 3 Seconds

[1] Based on PCB in feed

[2] None detected

[3] Run unsuccessful. Equipment plugged with SiO_2.

Solvent	1254 in sol. Combusted µg/ml	PCB's Destroyed %	% PCDFs Formed(1)				
			Cl_3	Cl_4	Cl_5	Cl_6	Cl_7
Mineral Oil	5000	82-88	0.72	0.58	0.17	-(2)	-(2)
Mineral Oil	500	87-92	0.4	0.33	0.084	-(2)	-(2)
Mineral Oil	50	88-90	0.3	0.3	0.056	-(2)	-(2)
C_2Cl_4	5000	68	0.44	1.50	1.35	0.33	0.50
C_2Cl_4	500	92	0.24	0.7	0.66	0.23	0.70
C_2Cl_4	50	72	0.44	1.32	1.0	0.38	0.16
Silicone(3)	-	-	-	-	-	-	-

The arcing and subsequent burning of an electrical transformer in a Binghamton State office building on February 5, 1981, produced the first recognized case in which toxic products, PCDDs and PCDFs, were produced outside of the laboratory from the combustion of chlorinated aromatic compounds in the transformer fluid (Schecter, 1986). Approximately 180-200 gallons of the transformer fluid, 65 % Aroclor 1254 and 35% tri- and tetrachlorinated benzenes, leaked from the overheated transformer in the basement of the building. The ensuing fire sent a dense cloud of smoke throughout the ventilation system of the building, resulting in contamination of the entire building. Initial sampling revealed levels of by-products to be 2,168,000 ppb of PCDFs, 20,000 ppb of PCDDs, and 50,000 ppb of polychlorinated biphenylenes. As a result of this incident, the U.S. Environmental Protection Agency declared that PCB-containing transformers must be replaced in many public buildings within the following few years. The impact on the health of exposed people was not the only consideration in making this ruling. The building itself was built at a cost of about 17 million dollars; the estimated cost of cleanup was 40 million dollars.

The assessment of the impact of such accidents upon the environment as well as mankind is greatly hindered by the difficulties encountered in the analysis of the emissions. Tables LXIV and LXV show the results from two different reputable laboratories which were obtained for analyses of the same samples or split samples. In Table LXIV, one laboratory reports a level of 2,3,7,8-Cl_4DF which is one-fifth that reported by the other laboratory and yet for the total Cl_6DF concentration, the former reports a level which is 17 times that as determined by the latter. This inconsistency of results is even more serious than that reported in Table LXV where at least one of the two laboratories gave consistently higher results than the other. The differences in the reported results does not reflect the inefficiency of the laboratories involved in determining the levels of PCDFs present, but rather it illustrates the difficulties inherent with such analyses.

Table LXIV: Comparison of Battelle vs. New York State Department of Health (NYSDOH)

Sample	2,3,7,8-Cl_4DF	Total Cl_4DF	Total Cl_5DF	Total Cl_6DF
BSOB Wipe, Stair Tread PCDD W-13 (NYSDOH 43968) Floor 16-17	5,900	45,000	99,000	41,000
BSOB Wipe, Stair Tread PCDD W-14 (Battelle) Floor 16-17	29,500	145,000	117,000	60,700
BSOB Wipe, Vinyl Wall W-7 (NYSDOH 43969)	1,100	13,000	8,500	2,000
BSOB Wipe, Vinyl Wall PCDD W-6 (Battelle)	1,320	4,980	820	120

Table LXV: Binghamton State Office Building
Test Plan: Measurements of Residual Contaminants Report
September 5, 1984
Polychlorinated Dibenzofuran Analysis Laboratory Comparison (Single extract)

Substances	Stalling 1981 [μg/g]	Rappe 1981 [μg/g]	Factor
2,3,7,8-Cl_4DF	3.7	12	3.2
Cl_4DF	5.4	28	5.1
Cl_5DF	107		
Cl_6DF	512		
Cl_7DF	102	460	4.5
Cl_8DF	30	40	1.3

The analytical results of some major PCB transformer and capacitor fires which occurred within the U.S. are summarized in Table LXVI (des Rosiers, 1986; des Rosiers, 1987). This list is representative of the cases in which efforts were made to determine the levels of PCDDs and PCDFs present. Of the fires listed, the Binghamton transformer fire is the only one in which PCDDs were clearly identified. The presence of chlorinated benzenes in the transformer fluid and the intense heat of the fire provided conditions similar to those in earlier laboratory studies which produced PCDDs from the pyrolysis of chlorinated benzenes.

Wipe samples from the Columbus fire showed a very small amount of PCDDs, however none were quantitatively detected in the corresponding soot samples analyzed. The capacitor oil was known to contain Aroclor 1242, however it is not known if any chlorinated benzenes were present to act as precursors for the formation of the trace levels of PCDDs found. The transformer involved in the San Francisco fire contained 100% Aroclor 1242 and no PCDDs were detected in the soot samples analyzed. Thus the presence of chlorinated benzenes appears to be necessary for the formation of PCDDs.

Table LXVI: Some Major Fires Involving PCB Transformers and Capacitors in the United States

PLACE	ANALYSES	PCDFs	PCDDs	COMMENTS	REFERENCE
Binghamton, NY State Office Building (2-15-81) (Transformer)	Soot Samples	Total PCDFs: 765-2160 ug/g 2,3,7,8-TCDF: 12-270 ug/g	Total PCDDs: 20 ug/g 2,3,7,8-TCDD: 0.6-2.0 ug/g	Transformer filled with 1060 gals. of Pyranol (65% PCBs) (Aroclor 1254) & 35% tri- and tetrachlorinated benezenes. Very hot fire, explosion & rupture of transformer with release of 180 gals. of fluid.	(4,5)
Cincinnati, OH Elementary School (12-3-80) (Capacitor)	Wipe Samples	ND	ND	Only 0.088 ml of PCBs (Aroclor 1254) was involved in the capacitor but the entire basement was contaminated at a mean level of 771 ug/100cm^2	(6)
Boston, MA Office Building (1-82) (Transformer)	Soot Samples	Total PCDFs: 165 ug/g 2,3,7,8-TCDF: 3 ug/g	ND	Transformer containing Aroclor 1254	(7)
Miami, FL Vault (4-3-82) (Transformer)	Soot Samples and Fire Residues	CDFs: 100-1000 ug/g	ND	Underground transformer vault	(8)
San Francisco, CA (Adj to High Rise) (5-15-83) (Transformer)	Wipe Samples	TCDFs - 15.6 ug/g	ND	3 transformers with 100% Aroclor 1242. No chlorobenzenes. 50 gals were released & smoldered for 8 hours after discovery.	(9)
Columbus, OH Office Building (3-84) (Capacitor)	Wipe Samples	Total PCDFs: up to 10,000 ng 2,3,7,8-TCDF: up to 1000 ng	Total PCDDs: up to 44 ng 2,3,7,8-PCDD: up to 3.0 ng	Capacitor with Aroclor 1242	(10,11
	Soot Samples	Total PCDFs: 10.9 ug/g	Total PCDDs: trace (tetra to octa). Trace amount of chlorobenzene. (Detection limit at ug/g level).		

Reproduced from best available copy.

The lack of analytical data regarding the nature of oil in the transformers or capacitors involved in fires makes evaluating data from wipe and soot samples difficult. Table LXVII lists the results of analyses of the oil samples taken from fires in three parts of the U.S. No PCDDs were detected in any of the oils (detection limit of 10 ng/g) and total PCDFs were typical of the levels found in stock materials previously studied. Normal use of electrical equipment therefore does not appear to produce PCDFs. PCBs and diluents such as chlorinated benzenes must be subjected to thermal stress in the presence of oxygen to produce PCDDs and PCDFs.

Table LXVII: Analysis of Fluids Involved in Transformer Fire Incidents

	Miami, FL[1] (May 29, 1984) (ug/g)	Binghamton, NY[2] (February 5, 1981) (ug/g)	Chicago, IL[3] (September 28, 1983) (ug/g)
PCDDs	ND	ND	ND
PCDFs (Total)	6.0	16.2	3.0
Tetra-CDF	0.31	0.48	<0.01
Penta-CDF	0.78	1.1	0.053
Hexa-CDF	2.2	11.0	0.47
Hepta-CDF	1.3	3.2	1.4
Octa-CDF	1.4	0.41	1.1
Chlorobenzenes (Total)	430,000	350,000	160,000
Trichlorobenzenes	260,000[a]	230,000[a]	100,000[a]
Tetrachlorobenzenes	140,000[a]	110,000[a]	51,000[a]
Pentachlorobenzenes	29,000[a]	13,000[a]	5,500[a]
Hexachlorobenzene	900[c]	45[c]	64[b]
PCBs (Total)	410,000	580,000	110,000[b]
Monochlorobiphenyls	320[b]	230[b]	<100[b]
Dichlorobiphenyls	1,100[b]	730[b]	<150
Trichlorobiphenyls	2,600[b]	3,500[c]	<200
Tetrachlorobiphenyls	2,000[b]	88,000	<400
Pentachlorobiphenyls	31,000[b]	300,000	11,000
Hexachlorobiphenyls	160,000[b]	160,000[c]	49,000[b]
Heptachlorobiphenyls	170,000[b]	24,000	45,000
Octachlorobiphenyls	32,000[b]	<800	7,300
Nonachlorobiphenyls	14,000	<1,200	<1,600
Decachlorobiphenyl	<2,800[b]	<3,500	<4,700

[a] Results of analysis at a dilution of 0.1 mg of oil/ml of hexane.
[b] Results of analysis at a dilution of 2.5 mg of oil/ml of hexane.
[c] Results of analysis at a dilution of 0.25 mg of oil/ml of hexane.

[1] Askarel Type A: 60% PCBs with 60% chlorine (Aroclor 1260) with 40% trichlorobenzene mixture.
[2] Askarel Type D: 70% PCBs containing 54% chlorine (Aroclor 1254) and 30% trichlorobenzene mixture.
[3] Mineral Oil with 25% PCBs (Aroclor 1260).

Lindane (γ-hexachlorocyclohexane, HCH) manufacturing wastes have been converted to predominantly 1,2,4-trichlorobenzene (TCB) which after purification by distillation was transformed to 1,2,4,5-tetrachlorobenzene for use in preparing 2,4,5-trichlorophenol (des Rosiers, 1987). The process involved the use of low temperature pyrolysis (200-240 °C) of the HCH wastes in the presence of a carbon catalyst in a closed reaction mantle. Residues from the mantle and the trichlorobenzene still were analyzed and were found to contain PCDDs and PCDFs (see Table LXVIII). The presence of oxygen during the pyrolysis and/or distillation of chlorinated aromatics can lead to the formation of dioxins and furans.

Table LXVIII: Dioxin Isomer Differentiation for Pyrolyzed HCH Residues and TCB Stillbottoms

Dioxin Isomer	Concentration [mg/kg] [ppm]
2,3,7,8-Cl_4DD	0.3
Cl_4DD	12
1,2,3,7,8-Cl_5DD	7
Cl_5DD	200
1,2,3,4,7,8-Cl_6DD	45
1,2,3,6,7,8-Cl_6DD	150
1,2,3,7,8,9-Cl_6DD	65
Cl_6DD	680
1,2,3,4,7,8,9-Cl_7DD	1,400
1,2,3,4,6,7,8-Cl_7DD	3,000
Cl_8DD	7,600

At a metal recovery site, salvaging of transformers was performed from 1972 to 1983 (des Rosiers, 1987). PCB-contaminated oil was burned in a stove and later analyses revealed the formation of PCDDs and PCDFs. The results of analyses performed on various samples at this site are given in Table LXIX.

Table LXIX: PCBs/PCDD/PCDF Analysis of Various Samples from the Strandley Site in Washington

Sample	PCBs [ppm]	PCDF [ppm]		PCDD [ppm]	
Soil	5 - 1,200	---		---	
Sediment	5 - 88	---		---	
Oil Sludge	5,600	---		---	
Water	4.7	---		---	
Burn area under Container	---	---		8.7	Cl_8DD
Ash on roadway bank	---	13	Cl_4DF	ND	Cl_4DD
		62	Cl_5DF	4.2	Cl_5DD
		91	Cl_6DF	1.8	Cl_6DD
		90	Cl_7DF	25	Cl_7DD
		55	Cl_8DF	43	Cl_8DD
Ash from stove in shop		545	Cl_4DF	178	Cl_4DD
		2,000	Cl_5DF	845	Cl_5DD
		2,300	Cl_6DF	1,100	Cl_6DD
		2,000	Cl_7DF	2,000	Cl_7DD
		320	Cl_8DF	890	Cl_8DD

At another scrap metal salvaging site, a small incinerator was used to burn PCBs and also provide heat to the surrounding residential community. Dust samples taken from within the building housing the incinerator were found to contain PCDFs and PCDDs, the latter being present in lower levels as indicated in Table LXX.

Table LXX: Dioxin and Furan in Dust Samples from Wire Recovery Site, Pittsburgh, PA

Homologue	Concentration [ng/g]
Cl_4DD	17 - 59
2,3,7,8-Cl_4DD	0.79 - 2.5
Cl_4DF	413 - 1,232
2,3,7,8-Cl_4DF	74 - 241

The U.S. Environmental Protection Agency (EPA) has concluded that:

1. PCDDs and PCDFs are not produced in PCB-containing transformers under normal operating conditions
2. Electrical arcings in transformers do not result in the formation of PCDDs and PCDFs
3. The amount of PCDFs formed as well as the particular isomers produced are related to the concentration and types of PCBs present in the transformer fluid
4. Chlorinated benzenes must be present in transformer fluids for PCDDs to be formed.

Considerable controversy has been generated by instances such as the accidental PCB transformer fire which occurred in Reims, France on January 14, 1985 (Abenhaim et al., 1987). In such cases, questions raised include:

1. What are the chemical substances involved?
2. At what concentrations are these substances present?
3. What are the exposure risks associated with the types and levels of potentially toxic materials present?

In order to help provide some of the answers to these questions, samples are invariably collected for analysis. The results of these analyses can further complicate matters as exemplified in the case of the fire in Reims. The analytical results obtained from several laboratories which analyzed the same soot sample are given in Table LXXI. The levels reported show tremendous deviation from one another. Analytical techniques employed today are extremely sensitive, however are not completely free of interference or errors in interpretation. There is an obvious need for better inter-laboratory analyses, most of which can be attributed to the lack of standard, validated analytical protocols.

Table LXXI: PCDD/PCDF Analyses (Fire in Reims); Interlaboratorial Comparison

PCDD/PCDF	Lab. #3 Sample 1 [µg/m²]	Lab. #4 Sample 5 [ng/g]	Lab. #5 Sample 5 [ng/g]	Lab. #6 Sample 5 [ng/g]
Cl_4DD		35,000	220	490
Cl_5DD	330	58,000	420	820
Cl_6DD	> 500	25,000	25	190
Cl_7DD	> 900	8,000	110	4
Cl_8DD	70	3,000	160	14
Cl_4DF	Not analysed	56,000	45	ND
Cl_5DF	Not analysed	81,000	150	550
Cl_6DF	Not analysed	7,000	490	45
Cl_7DF	85	8,000	210	Not detectable
Cl_8DF	65	8,000	350	Not detectable

VI. COMBUSTION OF WOOD

The emission of PCDDs and PCDFs resulting from the residential combustion of untreated wood has been studied (Clement et al. 1985). Samples of bottom and chimney ashes were collected from two wood burning stoves and an open fireplace. A sample of bottom ash was also collected from an out-door open-air burning of untreated wood. The samples collected are summarized in Table LXXII and the concentrations of PCDDs and PCDFs found in the various ash samples are given in Table LXXIII. PCDDs were detected in all of the samples analyzed. PCDFs were found in all of the ashes analyzed with the exception of one of the chimney ash samples. The relative amounts of the different congeners varied considerably from sample to sample, including the samples taken from the same wood burning stove (WB1-a and WB1-b). Perhaps the most important result of this study is the observation that the total levels of PCDDs and PCDFs found in the ashes are significantly lower than the levels typically observed for fly ash samples taken from municipal waste incinerators.

Table LXXII: Sample Description

Sample ID	Sample Type	Description	Type of Wood Burned
OA	Bottom Ash	Outside Open-Air Burning	Primarily Oak some paper used
CA-WB1	Chimney Ash	From Chimney above damper of WB1-a	same as OA
WB1-a	Bottom Ash	From Wood Burning stove	same as OA
WB1-b	Bottom Ash	Same stove as WB1-a, one year later	same as OA
WB2	Bottom Ash from WB1-a	From Wood Burning stove Different stove & location	75-80 % poplar
CA-FP	Chimney Ash	From Chimney above damper of FP	Unspecified
FP	Bottom Ash	Fireplace in home	Same as CA-FP

Table LXXIII: PCDD/PCDF from Wood Burning

* number in parentheses are numbers of isomers observed

ND = Not detected at average single-isomer detection limits of 10 ppt (pg/g) for Cl_4- and Cl_5 congeners, and 50 ppt for Cl_6-, Cl_7- and Cl_8DDs and -DFs

** recoveries could not be calculated; for these samples data are reported uncorrected

Congener	Concentrations in nanograms/gram (ppb)*						
	OA	CA-WB1	WB1-a	WB1-b	WB2	CA-FP	FP
4CDD	0.8(5)	ND	ND	0.1(4)	0.1(2)	ND	ND
5CDD	4.2(a)	ND	ND	3.0(10)	0.2(4)	0.5(6)	ND
6CDD	7.2(6)	ND	ND	10(6)	0.7(6)	1.7(6)	0.3(6)
7CDD	11(2)	0.1	0.3(2)	1.2(2)	0.5(2)	0.5(2)	2.0(2)
8CDD	10	0.2	2.6	0.9	0.1	0.4	3.1
TOTAL	33	0.3	2.9	15	1.6	3.1	5.4
4CDF	2.2(11)	ND	9.1(9)	0.4(12)	0.1(11)	0.3(8)	ND
5CDF	7.6(11)	ND	2.2(7)	4.6(9)	0.2(3)	1.4(8)	ND
6CDF	8.2(10)	ND	1.0(2)	9.3(8)	0.5(7)	1.7(5)	0.1(4)
7CDF	11(4)	ND	0.7(1)	1.0(4)	0.3(3)	0.4(3)	0.4(4)
8CDF	1.7	ND	ND	0.1	ND	0.1	0.1
TOTAL	31	ND	13	15	1.1	3.9	0.6
% recoveries							
^{13}C-1,2,3,4-TCDD	55	**	**	15	60	25	80
^{13}C-OCDD	41	47	**	92	43	58	67

* numbers in brackets are numbers of isomers observed

ND = not detected at average single-isomer detection limits of 10 pg/g (parts-per-trillion) for tetra and penta congeners, and 50 ppt for hexa, hepta and octachlorinated dibenzo-p-dioxins (CDD) and dibenzofurans (CDF).

** Recoveries could not be calculated; for these samples data are reported uncorrected.

Chimney soot samples from house heating in the area of Bayreuth, Germany, have been analyzed for PCDD/PCDF (Thoma, 1988a; Thoma 1988b)). High concentrations of PCDD/PCDF could be detected in chimney soots from 15 heating systems, two ovens fueled with wood/coal, 4 central heatings fueled with wood, and 9 ovens fueled with wood. The average concentrations of PCDD/PCDF of chimney soot are shown in Table LXXIV. A difference between oven and central heating was not detected. The PCDD/PCDF contents of chimney soot from combined wood/coal burning was 5 times less than those of wood and coal burning stoves; but definite conclusions cannot be drawn since only two samples have been analyzed. The results (for fossil fuels, see Chapter VII) showed that house heating is a major source of PCDD/PCDF and that concentrations from wood and coal burning systems are in the range of fly ash from municipal waste incinerators.

Table LXXIV: Average Concentrations of PCDD/PCDF in Chimney Soot [ppt]

Substance	Wood	Wood	Wood/Coal
Cl$_4$DD	31,279.3	10,301.4	2,410.0
Cl$_5$DD	21,167.3	25,979.5	1,325.0
Cl$_6$DD	23,264.3	18,309.0	609.1
Cl$_7$DD	39,689.0	13,635.0	465.5
Cl$_8$DD	51,480.8	10,639.2	312.3
Cl$_4$DF	162,696.5	76,279.7	31,300.0
Cl$_5$DF	260,400.0	91,048.0	8,065.0
Cl$_6$DF	76,953.0	56,885.9	2,335.0
Cl$_7$DF	13,848.0	13,281.5	600.6
Cl$_8$DF	2,832.3	7,268.2	146.1
2,3,7,8-Cl$_4$DD	310.1	420.7	121.2
1,2,3,7,8-Cl$_5$DD	1,429.1	860.9	107.3
1,2,3,4,7,8-Cl$_6$DD	886.9	967.7	21.8
1,2,3,6,7,8-Cl$_6$DD	1,415.2	1,399.6	63.6
1,2,3,7,8,9-Cl$_6$DD	1,262.5	1,205.0	53.5
1,2,3,4,6,7,8-Cl$_7$DD	22,065.0	7,507.4	253.3
2,3,7,8-Cl$_4$DF	11,294.3	9,374.2	1,900.0
1,2,3,7,8-Cl$_5$DF	19,658.8	10,879.5	646.6
2,3,4,7,8-Cl$_5$DF	34,818.8	10,589.0	1,287.8
1,2,3,4,7,8-Cl$_6$DF	9,422.4	4,248.6	273.1
1,2,3,6,7,8-Cl$_6$DF	8,672.9	3,262.7	251.7
1,2,3,7,8,9-Cl$_6$DF	588.9	392.2	18.3
2,3,4,6,7,8-Cl$_6$DF	4,665.1	2,200.7	100.6
1,2,3,4,6,7,8-Cl$_7$DF	8,000.6	9,230.9	377.9
1,2,3,4,7,8,9-Cl$_7$DF	1,008.3	909.2	48.1

The results of some earlier studies on treated wood are summarized in Table LXXV (Ontario Ministry of the Environment, 1985). Most of these studies were conducted in pilot scale incinerators although a few studies were done on open-air burning. In pilot scale studies, the PCDD emissions were found to decrease with increasing temperature and also with increasing residence time. These findings are similar to those reported for hazardous waste incinerators.

Table LXXVI lists the results of studies carried out on the combustion of untreated wood (Ontario Ministry of the Environment, 1985). Rudling et al. were not able to detect Cl_4DDs and Cl_4DFs in a wood-fire heating unit, a fireplace, and an airtight stove. Later studies conflicted with this report as PCDDs and PCDFs were found in numerous burnings of wood carried out under a range of conditions.

Table LXXV: PCDD/PCDF Concentrations in Combustion Effluents from the Combustion of Chemically Treated Wood/Wood Products

REFERENCE	MATERIAL COMBUSTED	COMBUSTION CONDITIONS	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
Jansson et al. (1978)	Commercial potassium 2,4,6-trichlorophenolate (36% 2,4,6-T_3CP, 40% T_4CP)	Pilot Scale Incinerator mixed with sawdust and burned with wood chips 580°C	Gas & Particulates (ug/g formulation used)	230	74	9	8	6					
		600°C		2.5	1.2	0.2	0.6	0.7					
		840°C		1.8	1.4	<0.4	ND	ND					
		OPEN FIRE		100	81	7	<1	<1					
	sodium 2,3,4,6-tetrachlorophenolate (6% 2,4,6-T_3CP, 31% T_4CP and 3% P_5CP)	(as above) 510°C	Gas and particulates (ug/g formulation used)	140	240	360	95	<2					
		690°C		10	43	53	10	ND					
		850°C		ND	14	17	ND	ND					
		OPEN FIRE		47	160	270	58	<5					
	pentachlorophenol 29% 2,3,4,6-T_4CP; 4.3% PCP	(as above) 515°C	Gas and particulates (ug/g of formulation used)	<0.2	<0.2	0.4	1.5	1.7					
		710°C		<0.2	<0.05	0.8	<0.2	<0.04					
		800°C		<0.2	0.5	0.6	<0.4	<0.08					
		OPEN FIRE		<0.2	0.9	2.0	9.0	19.0					
Reppe et al. (1978) Cont'd	Severex on wood wool	as above	Smoke and gases (ug/g chlorophenate used)	96-210	120-357	110-347	29-65	1.2					
Chiu et al. (1983) Williams (1982)	PCP impregnated wooden boxes	Open Air Burning (Ave. of 3 tests)	Particulate (ug/g)	0.002	0.014	0.118	0.083	0.187	ND	ND	TR	TR	0.025
			ng/dscm	1.7	3.7	42	27	61			TR	TR	8.2
			Gaseous ng/dscm	ND	ND	ND	ND	3	ND	ND	ND	ND	TR
Olie et al. (1983)	60 year old painted wood	Pilot scale Incinerator (Fluidized bed oven)	Fly ash (ug/g)	0.029	0.044	0.055	0.020	0.029	0.105	0.066	0.026	[illegible]	0.008
	PCP treated new wood		Fly ash (ug/g)	0.047	0.061	0.115	0.043	0.058	0.097	0.072	0.042	0.019	0.011
	Hypochlorite treated paper		Fly ash (ug/g)	0.001	0.003	0.009	0.007	0.004	0.004	0.002	0.003	0.002	0.001
Tiernan et al. (1983b)	wood (pine) plus HCl vapor	Micro-scale laboratory pyrolysis (with air)	Combustion products (ug/g of wood burned)	0.020	0.005	0.010	0.070	0.050	0.140	0.055	0.220	1.20	0.40

Table LXXVI: PCDD/PCDF Concentrations in Combustion Effluents from the Combustion of Untreated Wood

REFERENCE	MATERIAL COMBUSTED	COMBUSTION CONDITIONS	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
DOW Chemical Co. (1978)	Birch, oak, willow, ash and apple, plus some paper	Fireplace - A	Soot scrapings (ng/g)	0.37 (0.1)*		3.4	16	25					
	Hardwood - mostly oak	Fireplace B	Soot scrapings (ng/g)	ND(<0.04)(ND)*		0.23	0.67	0.89					
Rudling *et al.* (1980)	60:40 deciduous: coniferous wood	35 Kw central heating furnace with a pre-chamber	Gases and particulates (ng/g)	(ND)*					(ND)**				
	as above	as above with pre-chamber disconnected	Gases and particulates (ng/g)	(ND)*					(ND)**				
	50:50 deciduous: coniferous wood	Fireplace stove with glass shutters	Gases and particulates (ng/g)	(ND)*					(ND)**				
	as above	air tight stove with fan and heat exchanger	Gases and particulates (ng/g)	(ND)*					(ND)**				
Nestrick & Lamparski (1982)	Red oak	Residential Wood Stoves USA Eastern Region - USA	Partic. from chimney (ng/g) (Low)	0.002(<0.0006)*		0.021	0.063	0.095					
			(High)	7.8 (0.16)*		5.6	5.4	7.2					
			(Ave.)	2.0 (0.066)*		2.2	2.1	2.0					
	fir, oak	Western Region - USA	Partic. from chimney (ng/g) (Low)	0.093 (0.006)*		1.3	0.96	0.49					
			(High)	0.514 (0.02)*		9.2	5.8	5.2					
			(Ave.)	0.269 (0.013)*		4.3	3.2	2.2					
	ash, birch, oak	Central Region - USA	Partic. from chimney (ng/g) (Low)	<0.0001(0.0008)*		0.003	0.013	0.024					
			(High)	3.8 (0.2)*		65.3	39.0	37.0					
			(Ave.)	1.5 (0.006)*		14.2	12.6	13.8					
Clement *et al.* (1984)	Oak and paper	Outside air burning	Bottom ash	0.8	4.2	7.2	11	10	2.2	7.6	8.2	11	1.7
		Wood-burning stove	Chimney ash above damper	ND	ND	ND	0.1	0.2	ND	ND	ND	ND	ND
			Bottom ash ( ) same location one year later	ND(0.1)	ND(3.0)	ND(10)	0.3(1.2)	2.6(0.9)	9.1(0.4)	2.2(4.6)	1.0(9.3)	0.7(1.0)	ND(0.1)
	75% - 80% Poplar	Wood-burning stove	Bottom ash	0.1	0.2	0.7	0.5	0.1	0.1	0.2	0.5	0.3	ND
	unknown	Open fireplace	Chimney ash above damper	ND	0.5	1.7	0.5	0.4	0.3	1.4	1.7	0.4	0.1
			Bottom ash	ND	ND	0.3	2.0	3.1	ND	ND	0.1	0.4	0.1

( )* - 2,3,7,8-T_4CDD specific analysis.

( )** - 2,3,7,8-T_4CDF specific analysis.

Reproduced from

VII. FOSSIL FUEL COMBUSTION

There is conflicting and limited data regarding PCDD/PCDF formation by the burning of fossil fuels, mostly of coal. In some investigations polychlorinated dioxins were detected in ppb-amounts (Kimble and Gross, 1980; American Society of Mechanical Engineers, 1981).

PCDD/PCDFs are probably formed at low levels during burning of untreated wood after being logged (Lao). Compared to municipal waste incinerators the emissions are found to be in the same range (Umweltbundesamt, FRG, 1985).

In the soot of private heating systems dioxins were found to be present but at significantly lower levels than those detected in fly-ash (Table LXXVI) (Thoma, 1987; Hutzinger and Fiedler, 1987).

Table LXXVI: Concentration of PCDD/PCDF in the Soot of Home Heating; Concentration in [ppb]

Compound	MWI Fly Ash	Home Heating Soot Oil	Home Heating Soot Coal/Wood
Cl_4DD	19.06	3.90	1.54
Cl_5DD	37.25	0.41	5.13
Cl_6DD	115.49	3.06	5.20
Cl_7DD	275.88	1.37	2.76
Cl_8DD	598.69	1.05	2.37
Cl_4DF	79.45	28.91	50.80
Cl_5DF	120.30	16.55	30.04
Cl_6DF	116.34	6.24	11.67
Cl_7DF	108.24	1.78	3.23
Cl_8DF	42.90	0.33	0.53
2,3,7,8-Cl_4DD	0.60	0.10	0.21
2,3,7,8-Cl_4DF	2.47	1.07	1.92

Based on the results of these few studies, it appears that only coal-fired plants produce significant levels of PCDDs and PCDFs. It also appears that the total PCDF emission is greater than the total amount of PCDDs emitted. Further work must be done to confirm these findings.

Chimney soot samples from house heating have been analyzed for its content of PCDD/PCDF (Thoma, 1988a; Thoma, 1988b). The average concentrations found in soot samples from 21 central heating systems, 7 ovens both fueled with oil and 7 ovens fueled with coal are given in Table LXXVII. All samples from oil burning systems had detectable levels of PCDD/PCDF, but the concentrations from central heating were, on average, 10times less than in the samples of oil ovens. Generally, individual values varied within a factor of 10 to 100. In comparison to fly ash from municipal waste incinerators the concentrations in chimney soot were 10 to 100times lower.

The analyses of coal fired stoves revealed high levels of PCDD/PCDF and were in the range of those found in municipal waste incinerators and thus 10 to 100times higher than those of oil burning.

Table LXXVII: Average Concentrations of PCDD/F in Chimney Soot from Oil and Wood Fired Home Heating Systems [ppt]

Substance	Oil (Central Heating)	Oil (Oven)	Coal (Oven)
Cl_4DD	276.1	1633.8	11949,4
Cl_5DD	274.1	1681.0	7961.7
Cl_6DD	220.2	2393.4	11953.3
Cl_7DD	210.9	2712.9	11447.3
Cl_8DD	219.1	2,353.6	15,416.4
Cl_4DF	2,040.9	12,714.7	73,321.9
Cl_5DF	1,395.1	10,925.6	67,809.0
Cl_6DF	575.5	5762.1	25,493.9
Cl_7DF	243.3	2,444.4	6,329.2
Cl_8DF	98.8	598.2	839.5
2,3,7,8,-Cl_4DD	10.3	54.4	319.6
1,2,3,7,8-Cl_5DD	14.4	177.5	838.8
1,2,3,4,7,8-Cl_6DD	8.5	101.2	434.5
1,2,3,6,7,8-Cl_6DD	20.7	154.4	610.2
1,2,3,7,8,9-Cl_6DD	14.3	202.5	589.3
1,2,3,4,6,7,8-Cl_7DD	115.5	1,541.0	6,575.1
2,3,7,8-Cl_4DF	175.4	774.3	8,407.5
1,2,3,7,8-Cl_5DF	116.3	831.4	5,333.2
2,3,4,7,8-Cl_5DF	154.1	971.7	9,120.5
1,2,3,4,7,8-Cl_6CDF	79.4	732.6	3,292.6
1,2,3,6,7,8-Cl_6DF	58.8	655.3	3,176.5
1,2,3,7,8,9-Cl_6DF	6.3	68.7	211.7
2,3,4,6,7,8-Cl_6DF	34.3	411.4	1,339.0
1,2,3,4,,6,7,8-Cl_7DF	162.4	1,653.0	4,142.6
1,2,3,4,7,8,9-Cl_7DF	14.0	151.4	393.4

Emissions of fossil fuel plants revealed concentrations of the lower chlorinated dibenzofurans being 4-6times the concentrations of the respective dioxins. Within both classes lower chlorinated isomers predominated the higher chlorinated compounds.

The studies on emissions from coal- and oil-fired power plants are summarized in Table LXXVIII covering the years 1978 to 1983 (Ontario Ministry of the Environment, 1985). The levels of PCDDs and PCDFs found in the fly ash were much lower than the levels reported in most municipal incinerator studies. No dioxins or furans were detected in the flue gas samples analyzed by Haile, however in a later study of two Canadian coal-fired plants, low levels were detected. The results of this later study are shown in Table LXXIX.

Table LXXVIII: PCDD/PCDF Concentrations in Effluents from Fossil Fuel Combustion

REFERENCE	MATERIAL COMBUSTED	COMBUSTION CONDITIONS	SAMPLE MATRIX (UNITS)	PCDD					PCDF				
				T_4	P_5	H_6	H_7	O_8	T_4	P_5	H_6	H_7	O_8
DOW Chemical Co. (1978)	coal and fuel oil	Industrial power plant	fly ash (pg/g)	38,000		2,000	4,000	24,000					
DeRoos & Bjorseth (1979)	coal	power plant	fly ash (pg/g)	ND(<1.5)									
Kimble & Gross (1980)	low sulphur, high ash coal	large modern power plant	fly ash (pg/g)	0.6									
Mahle & Whitting (1980)	bituminous coal+ air	Micro-scale laboratory	(pg/g coal)	ND(<80)		ND(2100)	570	1,300					
Malle *et al.* (1982)	pulverized coal	4 coal-fired utility power plants	fly ash (pg/g) flue gas(pg/m^3)	ND(<10) ND(<100)	ND(50) ND(500)	ND(<50) ND(<500)	ND(<70) ND(<700)	ND(<10) ND(<700)	ND(<10) ND(<100)	ND(<50) ND(<500)	ND(<50) ND(<500)	ND(<70) ND(<700)	ND(<70) ND(<700)
Harless & Lewis (1982)	coal	7 coal-fired power plants	fly ash (pg/g)	ND(<1.0-2.8)									
Nestrick & Lamparski (1982)	oil	residential oil furnace	flue pipe soot (pg/g)	ND(<2.4)		ND(<4.2)	25	130					
Chiu, *et al.* (1983)	coal	large modern coal-fired power plant	fly ash (pg/g)	1,000	6,000	6,000	5,000	ND	8,000	32,000	18,000	18,000	ND
		coal-fired central heating facility	fly ash (pg/g)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table LXXIX: Total Particulate - Phase Stack Emission Concentrations of PCDD and PCDF from Two Coal-Fired Sources * [dscm]

Source	Particulate-Borne Stack Emissions											
	PCDD						PCDF					
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Total	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Total
Large coal-fired power plant	0.1	0.1	ND	0.1	ND	0.3	0	1	2	ND	ND	3
Smaller coal-fired central heating facility	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

* measurements done in 1981

[dscm]dry standard cubic meter

VIII. COMBUSTION OF AUTOMOBILE FUELS

In a recent report, halogenated aromatic compounds, predominantly brominated, were identified in the emissions of automobiles fueled by leaded gasoline (Müller and Buser, 1986). Dibromoethane (DBE) and dichloroethane (DCE), which are added to leaded gasoline as scavengers to prevent deposition of lead compounds in engines, are believed to become involved in the many side reactions which take place in the engine. In unleaded gasoline, where no DBE or DCE are added, no halogenated aromatics were detected.

In another recent study, the presence of PCDDs and PCDFs in motor oil from diesel and gasoline fueled vehicles was reported (Ballschmiter et al., 1986). Incomplete combustion and the presence of a chlorine source in the form of additives in the oil or the fuel such as dichloroethane or pentachlorophenate may lead to the formation of PCDDs and PCDFs. The isomeric patterns of the dioxins and furans found in the motor oils were compared to those observed from municipal incinerator emissions. Some similarities were observed, however this does not yield any understanding of the mechanisms involved. The levels of PCDDs and PCDFs were not reported and thus the impact of this source to the environment is not known.

A comparison of the emissions resulting from the use of leaded and unleaded gasoline in automobiles was performed in an attempt to link the formation of PCDDs and PCDFs to the chlorinated scavenger additive (Marklund et al., 1987). The tests were carried out using two cars which were run on unleaded gasoline which contained no dichloroethane scavenger and on four cars run on leaded gasoline. The leaded gasoline was actually the same unleaded fuel but with the addition of 0.15 g/L of tetraethyllead and 0.1 g/L of dichloroethane. The normal scavenger mixture of DBE and DCE was not used in order to avoid the formation of mixed chloro/bromo dioxins and furans which would complicate the analyses due to the large number (>5000) of possible isomers. Carbon monoxide, hydrocarbon, and NO_x emissions were monitored and showed that all cars tested were in good condition and met the Swedish emission requirements.

The sampling was performed over two 12.4 km running cycles giving at total run distance of 24.8 km. The emissions resulting in the tests are summarized in Table LXXX. For the cars fueled by unleaded gasoline, no PCDDs or PCDFs were detected above the maximum detection limit of 0.3 ng. PCDDs and PCDFs were identified in all of the test cars run on leaded gasoline with the DCE scavenger. The total levels of PCDDs and PCDFs produced varied from car to car and therefore it is difficult to assess a representative level of emission resulting from the fuel combustion process. It should be noted that the same motor oil was used in all test cars thereby eliminating the possibility that the dioxins and furans were formed from additives or contaminants in the oil. The dichloroethane is most likely the source of the PCDDs and PCDFs formed, although it is possible that they were also formed in the cars run on unleaded gasoline and subsequently destroyed in the catalytic converter. The latter hypothesis seems unlikely but should be verified.

Based on their findings, the total emissions of PCDDs and PCDFs from all cars fueled by leaded gasoline would be equivalent to 2 to 20 municipal solid waste incinerators of average size and technology. These emissions are only considered for the exhausts produced. The levels of PCDDs and PCDFs in motor oil and in particulates found in mufflers still need tc be estimated.

Table LXXX: PCDD and PCDF in Car Exhausts [ng/24.8 km]

Compounds	Cars running on non leaded gasoline (n = 2)	Cars running on leaded gasoline (n = 4)
2,3,7,8-Cl_4DF	ND	0.6 - 13
Σ Cl_4DF	ND	10 - 200
2,3,7,8-Cl_4DD	ND	< 0.05 - 0.3
Σ Cl_4DD	ND	3 - 90
1,2,3,7,8-Cl_5DF	ND	0.5 - 4.6
2,3,4,7,8-Cl_5DF	ND	0.3 - 3.9
Σ Cl_5DF	ND	5 - 46
1,2,3,7,8-Cl_5DD	ND	0.5 - 3.5
Σ Cl_5DD	ND	6 - 98
Cl_4DD Equivalents	ND	0.8 - 13

Detection limits:

2,3,7,8-Cl_4DF	0.2 ng
2,3,7,8-Cl_4DD	0.05 ng
1,2,3,7,8/2,3,4,7,8-Cl_5DF	0.2 ng
1,2,3,7,8-Cl_5DF	0.3 ng

The exhaust emissions of six cars, driven through three or four cycles of the EPA urban driving cycle, have been analyzed for PCDD/PCDF (Bingham et al., 1988). Five of the cars were run on New Zealand high octane petrol containing a lead additive (0.45 g/L tetramethyllead, 0.22 g/L dichloroethane and 0.2 g/L dibromoethane). The sixth car was run on low octane lead additive-free petrol. The exhaust gases were proportionally (0.03 to 0.05 of the total inlet flow) sampled through a modified EPA Method 5 sampling train. Total Cl_4DF emissions have been detected in the range from Not determined - 1,5 ng/km for cars run on leaded fuel.

Exhaust gases from three different vehicles (two cars fueled with leaded and unleaded gasoline, respectively and a heavy diesel truck) were investigated for the presence of polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) (Haglund et al., 1988). The results (Table LXXXI) showed that leaded gasoline yields much more Br_4DD/Br_4DF than unleaded gasoline. The authors concluded that the dibromoethane added to this type of gasoline probably act as a halogen source. Generally, the levels of tetrabrominated dibenzodioxins and dibenzofurans found in this investigation were higher than the levels of the respective tetrachlorinated species reported in the above mentioned report (Marklund et al., 1987)

Table LXXXI: Analysis of PBDD/PCDF in Vehicle Exhaust

Compounds (unit)	Car leaded gasoline	Car unleaded gasoline	Car diesel oil	Detection limits	
				gasoline cars [ng/km]	diesel truck [ng/L fuel]
Br_2DF [ng/km]	1,100	ND	ND	2	28
Br_2DD [ng/km]	ND	ND	ND	20	260
Br_3DF [ng/km]	180	1.4	ND	0.08	1
Br_3DD [ng/km]	19	ND	ND	0.4	5
Br_4DF [ng/km]	23	0.24	ND	0.03	0.4
Br_4DD [ng/km]	3.2	ND	ND	0.3	3
Br_5DF [ng/km]	0.98	ND	ND	0.03	0.4

IX. PVC AS CHLORINE DONOR

PVC as chlorine donor in municipal waste incineration (Wilson, 1977) has been discussed discussed for a long time. New studies (Hawley-Fedder, 1984) and samples of fly ash from municipal waste incinerators fueled with high contents of PVC (Karasek et al., 1983) could not confirm PVC as source for the formation of high concentrations of PCDD/PCDF. Copper smelters and plants for metal recovery are to be considered separately, where cables covered with PVC are thermolyzed in the presence of e.g. copper (Hutzinger and Fiedler; 1988). The levels of PCDD/PCDF (in 100 ppb to ppm-range) found in the emissions (Eberhard and Friege, 1987; Bröker, 1987) may be due to catalytic inference of the metals present.

To get some more information on PVC as a source for the formation of PCDD/PCDF the products formed during combustion and pyrolysis of pure, commercial polyvinylchloride and PVC cable sheatings have been analyzed (Christmann et al., 1988). In simple laboratory experiments 2 g of a PVC sample were incinerated with a laboratory gas burner, the combustion products were condensed and collected on the inner walls of a cooled glas funnel placed upside down above the sample. The soot deposits were removed with toluene. Pyrolysis experiments were performed in a modified Schöninger apparatus with 50 g of PVC, heated to about 950 °C for 10 min in either air or nitrogen atmosphere. In another experimental set-up, the tip of a soldering iron was wrapped with a PVC-coated copper wire and heated for about 5 min to approximately 350 °C. In the gas-flame combustion of low molecular pure PVC PCDF were found in the low $\mu g/m^2$ range (1 $\mu g/m^2$ corresponds with 1 mg/kg) in the soot (Table LXXXIII). Similar results were obtained with PVC-cable coatings. High molecular PVC gave approximately 4times higher values of PCDF,preferably of lower chlorinated PCDF, but PCDD could be detected in case of pure PVC. The analysis of the soot from the combustion of cables coated with PVC gave low values of PCDD similar to those found after fires in public buildings. The pyrolysis of pure PVC as well as PVC-cable coatings yielded dioxins and furans in the lower mg/kg range (Table LXXXIV). Here also, furans were formed predominantly. Especially high values of hepta- and octa-chlorinated dioxins and furans, ranging up to the milligram level were formed in the pyrolysis of PVC-coated cables. In the experiments carried out in the Schöninger apparatus under a nitrogen atmosphere no detectable quantities of PCDD/PCDF were formed as well as in neither combustion or pyrolysis experiments with chlorine-free polyethylene samples dioxins or furans could be detected.

Table LXXXIII: Formation of PCDD/PCDF by Combustion of PVC [$\mu g/m^2$]

* GefStoffV: German statuatory regulation for dangerous substances, limit 5 µg/kg for the sum of eight labeled (*) congeners. Results related to soot.
** TE: Toxic Equivalents using TEF of the German Federal Health Office

PCDD/PCDF		pure PVC		PVC-cable	soot from a fire
		high molec.	low molec.		
TeCDD(2,3,7,8)	*	n.d.	n.d.	n.d.	n.d.
Su TeCDD		n.d.	n.d.	n.d.	0.2
PeCDD(1,2,3,7,8)	*	n.d.	n.d.	n.d.	n.d.
Su PeCDD		n.d.	n.d.	n.d.	0.2
HxCDD(1,2,3,4,7,8)	*	n.d.	n.d.	0.14	n.d.
HxCDD(1,2,3,6,7,8)	*	n.d.	n.d.	0.12	n.d.
HxCDD(1,2,3,7,8,9)	*	n.d.	n.d.	0.10	n.d.
Su HxCDD		n.d.	n.d.	0.36	0.4
HpCDD(1,2,3,4,6,7,8)		n.d.	n.d.	0.4	0.3
Su HpCDD		n.d.	n.d.	0.14	0.4
OCDD		n.d.	n.d.	0.09	0.2
TeCDF(2,3,7,8)	*	n.d.	0.04	0.38	0.2
Su TeCDF		9.24	2.53	2.29	3.2
PeCDF(1,2,3,7,8)+(4,8)		0.65	0.17	0.35	0.3
PeCDF(2,3,4,7,8)	*	0.36	0.09	0.26	0.2
Su PeCDF		5.36	0.98	1.76	1.5
HxCDF(1,2,3,4,7,8)+(7,9)		0.71	0.18	0.30	0.2
HxCDF(1,2,3,6,7,8)	*	0.43	0.11	0.22	0.1
HxCDF(1,2,3,7,8,9)		0.06	n.d.	0.08	0.1
HxCDF(2,3,4,6,7,8)		0.24	n.d.	0.14	0.1
Su HxCDF		3.73	0.89	1.34	0.8
HpCDF(1,2,3,4,6,7,8)		1.55	0.40	0.43	0.2
HpCDF(1,2,3,4,7,8,9)		0.30	0.08	0.12	0.1
Su HpCDF		2.67	0.72	0.77	0.5
OCDF		1.02	0.19	0.34	0.3
TE (BGA/UBA) **		0.45	0.11	0.27	0.19
Gef Stoff V * (µg/kg)		790	240	1220	550

Table LXXXIV: Formation of PCDD/PCDF by Pyrolysis of PVC [µg/kg]

PCDD/PCDF		Schöninger apparatus 950^{0}C				soldering iron 350^{0}C
		pure PVC		PVC-cables (n = 5)		PVC -coated copper wire
		high molec.	low molec.	min.	max.	
TeCDD(2,3,7,8)	*	n.d.	n.d.	n.d.	n.d.	n.d.
Su TeCDD		1	24	n.d.	n.d.	n.d.
PeCDD(1,2,3,7,8)	*	n.d.	n.d.	n.d.	n.d.	7
Su PeCDD		34	33		n.d.	151
HxCDD(1,2,3,4,7,8)	*	n.d.	n.d.	n.d.	n.d.	1
HxCDD(1,2,3,6,7,8)	*	n.d.	n.d.	n.d.	n.d.	13
HxCDD(1,2,3,7,8,9)	*	n.d.	n.d.	n.d.	n.d.	1
Su HxCDD		34	n.d.	n.d.	n.d.	167
HpCDD(1,2,3,4,6,7,8)		27	24	10	460	105
Su HpCDD		44	43	27	799	208
OCDD		493	19	14	1040	247
TeCDF(2,3,7,8)	*	n.d.	4	n.d.	n.d.	n.d.
Su TeCDF		124	199	63	115	127
PeCDF(1,2,3,7,8) + (4,8)		20	27	n.d.	6	17
PeCDF(2,3,4,7,8)	*	14	15	n.d.	5	1
Su PeCDF		47	190	24	370	112
HxCDF(1,2,3,4,7,8) + (7,9)		36	50	2	11	32
HxCDF(1,2,3,6,7,8)	*	32	35	n.d.	8	26
HxCDF(1,2,3,7,8,9)		7	7	n.d.	n.d.	6
HxCDF(2,3,4,6,7,8)		24	17	4	8	42
Su HxCDF		156	294	32	53	216
HpCDF(1,2,3,4,6,7,8)		147	215	54	1839	129
HpCDF(1,2,3,4,7,8,9)		30	37	n.d.	364	22
Su HpCDF		236	340	72	2857	199
OCDF		143	163	64	2016	58
TE (BGA/UBA) **		18.7	24.4		41	24
Gef Stoff V *		45	54		19	49

X. COMPARISON OF COMBUSTION SOURCES

Sheffield has been the only author who reviewed some years ago the emission sources of PCDDs and PCDFs in an attempt to estimate the levels of dioxins and furans introduced into the Canadian environment (Sheffield, 1985). From his information sources, he claimed that the largest source of PCDD emission came from forest fires. An estimated 60 kg per year are introduced into the environment from this source alone. This level was determined based on test results from residential wood combustion being extrapolated to fit the amount of wood burned during forest fires as estimated from a ten-year average. Other sources which show potentially significant releases of PCDDs and PCDFs include municipal incinerator fly ash and air emissions, sewage sludge incinerator air emissions, and the combustion of waste wood in wigwam burners and/or wood waste boilers. The estimated levels from each of these sources and other sources of PCDDs and PCDFs are given in Table LXXXV. The levels in these tables are based on preliminary estimates from the most recent data available (at that time) and are from tests done largely by Canadian institutions.

Precipitated fly ash and stack flue gas samples have been taken from several of the municipal incinerators operating in Canada. Municipal waste incineration has been the most studied source of PCDDs and PCDFs in Canada, however major variations exist in the reported data and therefore a wide range of yearly total emissions have been projected in Table LXXXV.

Precipitated fly ash samples were taken from Canadian coal-fired utilities show low concentrations of PCDDs and PCDFs. These levels appear to be at maximum lower than the lowest levels produced in municipal incinerators. The air emissions tested for one coal-fired plant were found to be very low and the total air emissions projected for coal-fired plants are approximately equal to the minimum levels estimated for municipal incineration. This projection must be taken with a degree of caution since the author of this work has extrapolated the results for one coal-fired plant to all such facilities in Canada. Variations from plant to plant may be observed as in the case of the municipal incinerators which have been studied.

As for coal-fired utility boilers and their air emissions, only one sewage sludge incinerator was tested and the results were extrapolated to give an estimate of yearly emissions for all such facilities in Canada.

Table LXXXV: PCDD and PCDF Released to the Environment, from Combustion Sources

Source	Releases [g/year] PCDD	PCDF
Municipal waste incinerators		
- Fly ash	2,900 - 7,100	4,900 - 15,600
- Air emissions	250 - 13,700	550 - 21,700
Sewage sludge incineration		
- Air emissions	1,400 - 3,300	1,500 - 6,500
Coal-fired utility boilers		
- Fly ash	ND - 300	30 - 1,300
- Air emissions	300	700
Fuelwood combustion		
- Air emissions	1,800	*
Residential oil combustion		
- Air emissions	< 1	*
Residential gas combustion		
- Air emissions	900	*
Wigwam burners/Wood waste boilers		
- Air emissions	0 - 30,200	
Railway ties		
- Air emissions	6,000	
Forest fires		
- Air emissions	58,700	*
Slash burning		
- Air emissions	3,300	*
Cigarette Smoke		
- Air emissions	2 - 4	*
Motor vehicles		
- Air emissions	200	*

* - not investigated

The estimated emissions from fuelwood combustion were derived from the average concentrations of PCDDs reported from American tests performed on residential wood combustion. The particulate emissions of such devices as determined from Canadian studies were used with the average PCDD concentration calculated from the American studies to give the estimate listed in table LXXXIII.

Residues from the wood protection and preservation industries, in the form of diptank sludges and wood shavings, can present a serious problem, especially when wastes contaminated with chlorinated phenols are incinerated in wigwam burners or wood waste boilers. As indicated in Table LXXXVI, significant variations in the levels of PCDDs and PCDFs emitted were found for various studies. Contradictory results have been reported ranging from no emission of PCDDs or PCDFs to significant emissions of these compounds being released. Therefore it is apparent that much more work needs to be done in the investigation of this potentially significant source of dioxins and furans.

The estimated emission of PCDDs from the burning of railway ties was determined based on data taken from studies concerning the combustion of pentachlorophenol-sprayed wood.

The results of the analyses of chimney soot samples (see Chapter VII, Fossil Fuel Combustion) have shown that house heating is a source for emission of PCDD/PCDF that should betaken into consideration (Thoma, 1988a, Thoma, 1988b). The German Hazardous Waste Regulations state that where the sum of 2,3,7,8-Cl_4DD, 1,2,3,7,8-Cl_5DD, 1,2,3,6,7,8-Cl_6DD, 1,2,3,7,8,9-Cl_6DD, 2,3,7,8-Cl_4DF, 2,3,4,7,8-Cl_5DF, and 1,2,3,6,7,8,-Cl_6DF exceed 5 ppb, the material has to be treated as hazardous waste (Chemikaliengesetz, 1988). Table LXXXVI summarizes the levels of these toxic isomers found in chimney soot from house heating.

Table LXXXVI: Average Concentrations of the Toxic PCDD/PCDF-Isomers in Chimney Soot from House Heating [ppt]

Substance	Oil (Heating)	Oil (Oven)	Coal (Oven)	Wood (Oven)	Wood (Oven)	Wood/Coal (Oven)
2,3,7,8-Cl_4DD	10.3	54.4	319.6	310.1	420.7	121.2
1,2,3,7,8-Cl_5DD	14.4	177.5	838.8	1,429.1	860.9	107.3
1,2,3,6,7,8-Cl_6DD	20.7	154.4	610.2	1,415.2	1,399.6	63.6
1,2,3,7,8,9-Cl_6DD	14.3	202.5	589.3	1,262.5	1,205.0	53.5
2,3,7,8-Cl_4DF	175.4	774.3	8,407.5	11,294.3	9,374.2	1,900.0
2,3,4,7,8-Cl_5DF	154.1	971.7	9,120.5	34,818.8	10,589.0	1,287.8
1,2,3,6,7,8-Cl_6DF	58.8	655.3	3,176.5	8,672.9	3,262.7	251.7
Total	448.0	2,990.1	2,306.4	59,202.9	23,849.4	3,785.1

The limits of 5 ng/g given by law is exceeded in chimney soots from wood and coal burning systems which implies that these soots should be treated like fly ash from municipal waste incinerators and be disposed of in special dump sites and not on municipal waste disposal sites. Until now there are no data to support the hypothesis that PCDD/PCDF emissions from household heating systems to the atmosphere potentially damage the environment, there is indirect evidence. Analysis of spruce needles from different regions revealed that the PCDD/PCDF concentrations in so-called 'clean' areas were 10times less only compared to those around municipal waste incinerators (Reischl, 1988). All these data indicate that diffuse sources such as house heating influence the background level of PCDD/PCDF.

The National Dioxin Strategy set by the United States Environmental Protection Agency (EPA) in December 1983 was established in order to (des Rosiers, 1986; Southerland et al., 1987; National Dioxin Study, 1987a, 1987b):

1. determine the overall extent of dioxin contamination in the environment
2. provide a systematic approach for dealing with dioxin decontamination problems.

The majority of the interest was centered around the most toxic dioxin, the 2,3,7,8-Cl_4DD isomer.

The National Dioxin Strategy was divided into seven different categories (referred to by the EPA as tiers). Tier 4 of the strategy dealt with studies conducted on the emission of dioxins and furans from a variety of combustion sources. The activities carried out in the Tier 4 study were focussed on those sources which were believed to have the greatest potential for emitting dioxins and furans. The sources were categorized and assigned testing priorities based on the information obtained from a literature review of relevant studies.

From the literature review it was concluded that the emission of PCDDs from combustion sources could be attributed to:

a) PCDDs present in the materials being burned

b) The presence of PCDD precursors (for example, chlorinated phenols and chlorobenzenes) in the materials burned

c) The presence of chlorine, fuel, and combustion conditions conducive to PCDD formation

d) relatively low combustion temperatures (500 to 800 °C)

e) short residence time in the combustion zone (less than 1-2 seconds)

f) lack of adequate oxygen resulting in incomplete combustion

g) lack of adequate processing of fuels (for example, burning wet garbage)

h) lack of supplemental fuel to promote combustion efficiency.

The literature review resulted in the identification of thirteen generalized combustion sources which have been found to emit PCDDs and PCDFs. These sources are:

1. municipal solid waste incinerators
2. sewage sludge incinerators
3. fossil fuel combustion
4. wood combustion
5. boilers co-firing wastes
6. hazardous waste incinerators
7. hospital incinerators
8. lime/cement kilns
9. wire reclamation
10. PCB fires
11. automobile emissions
12. activated carbon regeneration furnaces
13. experimental studies

The results of their literature review are summarized in Tables LXXXVII and LXXXVIII. Unfortunately it is extremely difficult to directly compare data reported by various laboratories due to the differences in the sampling and analytical procedures. The lack of source-specific information and intangibles such as the quality of the reported work also hinder this comparison.

After completing an initial literature review in October 1984, combustion sources were ranked according to their potential for emitting dioxins. These rankings are shown in Table LXXXVIX. Sources given a rank of "A" were expected to have the highest emission of dioxins. Ranks B and C have decreasing potentials for PCDD emission. Combustion sources classified as rank D have been previously subjected to a number of studies deemed to be sufficient by the EPA. When inputs from other agencies were considered, the list was modified for the reasons given in Table XC. Thus a final ranking was chosen for use in determining what sources would be studied in the Tier 4 program (see Table XCI). The objective of the program was to test each rank A source three times, each rank B source once, and as many rank C source as possible.

The thirteen test sites chosen for the study are briefly described in Table XCII. The mean combustion device operating parameters throughout the course of the test runs are summarized in Table XCIII. The PCDD/PCDF emissions data for the Tier 4 tests are outlined in the following discussion. A more detailed discussion is given in the project's engineering analysis report (EPA, 1987b).

The outlet flue gas emission concentrations are summarized in Table XCIV. This data represents average values for the outlet emission of 2,3,7,8-Cl_4DD as well as total PCDD and PCDF emissions. All flue gas concentrations were normalized to an oxygen level of 3 percent in order to minimize the effect of excess air dilution when comparing emissions from different sites. The combustion devices were ranked according to total PCDD emission.

Table XCIV also includes estimated values of the total emissions expressed in terms of 2,3,7,8-TCDD equivalents. These toxic equivalence estimations were used to compare the relative potency of the emissions from different sites. The toxic equivalent factors listed in Table XCV were used in calculating the 2,3,7,8-TCDD equivalent emission rates.

Table XCIV shows that dioxins and furans were found to be emitted by every source tested with the exception of the woodstove for which no valid data was available because of analytical problems encountered. Considerable variations in the average total PCDD and PCDF emissions were observed for this set of test sites. It should be noted however that the variations from test-to-test for each site were generally less than the site-to-site variations.

The total PCDD and PCDF emissions were found to be roughly the same order of magnitude for each of the sites tested, however for most sites the total PCDF emissions were higher than the total PCDD emissions.

Detectable levels of 2,3,7,8-Cl_4DD were found in the outlet emissions from seven of the test sites. The amount of 2,3,7,8-Cl_4DD contributed only a small percentage to the total PCDD concentration. The amount of 2,3,7,8-Cl_4DD relative to the total amount of dioxins emitted was found to vary considerably from one site to another.

The flue gas was also sampled at the inlet of air pollution control devices for some of the sites. The results of these analyses are shown in Table XCVI. Dioxins and furans were found in the inlet flue gas for all seven of the sites tested. For most sites the total PCDD/PCDF emissions were higher at the inlet of the pollution control device than at the stack outlet. This was also found to be true for the respective levels of 2,3,7,8-Cl_4DD. Higher levels are expected at the inlet since the pollution control devices are intended to remove dioxins and furans from the flue gas (and hence prevent them from escaping directly into the atmosphere). As for the outlet concentrations, the total levels of PCDDs and PCDFs are roughly the same order of magnitude although there tends to be a larger amount of furans in the flue gas.

The average mass emission rates (micrograms/hour) for the test sites are summarized in Tables XCVII and XCVIII. Table XCVII lists the outlet PCDD/PCDF mass emission rates while Table XCVIII gives the control device inlet mass flow rates. The ranking by average outlet total PCDD mass emission rate results in a different ranking than observed for Tables XCIV and XCVI. This is because of the differences in flue gas flow rates between sites.

The variation in PCDD/PCDF mass flow rates is much greater for the outlet emissions than for the control device inlets of the sites. The relationships between the emission rates of 2,3,7,8-Cl_4DD, total dioxins, and total furans for an individual test site are the same as those observed in Tables XCIV and XCVI since the mass emission rate is directly proportional to the mass emission concentration.

The mass emissions were scaled per unit of feed (µg/kg) by dividing the emission rates (µg/hr) by the rate of mass feed (kg/hr) to the combustion device. The scaled mass emissions for the outlet and inlet sites sampled are summarized in Tables CIX and C. The presence of dioxin and furan precursors in the input feed material was studied in order to investigate the influence of the combusted matter on the emissions of PCDDs and PCDFs. Specific compounds known to be PCDD or PCDF precursors were determined in the collected feed samples. The compounds analyzed for included chlorobenzenes, chlorophenols, and polychlorinated biphenyls. Total organic halogen (TOX) and total chloride content analyses were also performed on the feed samples for the various sites studied. The results of the precursor analyses are given in Tbale CI.

The homologue distribution patterns for the inlet and outlet flue gas samples for the combustion sites tested are graphically represented in Figures 43 through 51. From the study of the homologue distributions it was concluded that:

1. Each test site has a characteristic PCDD/PCDF homologue "fingerprint". Reasonably good precision between test runs was observed for an individual site. No correlation between the homologue distribution and the precursors in the feed material was apparent.

2. Considerable variation in homologue distribution patterns was observed amongst test sites.

3. Homologue distributions of PCDDs did not always resemble patterns observed for PCDFs for the same site.

4. Homologue distributions do not shift significantly across the control devices (for those in which both inlet and outlet emission data are available). This suggests that there are no significant differences in removal efficiencies for dioxin or furan homologues.

Based on the literature review, there are numerous variables which are suspected to influence the levels of the PCDD and PCDF emissions. The variables tested in the Tier 4 study are outlined in Table CII. The observations drawn from the data gathered from the inlet and outlet flue gas samples for the various sites are summarized below.

1. The outlet emissions of 2,3,7,8-Cl_4DD and total PCDDs are directly related but not proportionally. Sites having high levels of total PCDDs also have relatively high levels of 2,3,7,8-Cl_4DD. The same general trend is also observed for 2,3,7,8-Cl_4DF and total PCDF levels.

2. Excluding the secondary copper smelter (MET-A), there appears to be a correlation between the outlet flue gas total chloride concentration and the total outlet PCDD/PCDF emissions. For site MET-A the total dioxin and furan emission concentrations were extremely high yet relatively low flue gas total chloride concentrations were observed.

3. Other variables considered (such as maximum combustion temperature, CO, THC, total feed chloride, and TOX) did not show any significant correlation with the outlet emissions of dioxins and furans.

4. For the inlet flue gas, the total PCDD and PCDF concentrations appear to be inversely related to the maximum temperature.

5. Total PCDD and total PCDF emissions appear to be related since both are roughly of the same order of magnitude for each site tested. Sites emitting relatively high concentrations of PCDDs also emit relatively large amounts of PCDFs.

6. Other variables considered do not appear to show significant association with inlet flue gas PCDD and PCDF levels.

7. Maximum dioxin and furan flue gas concentrations for a given site appeared to be associated with higher TOX levels in the feed material.

8. Other variables did not appear to significantly influence maximum PCDD/PCDF flue gas concentrations for a given site.

Although these observations were made, they were not deemed to be conclusive. Further testing was recommended

Analysis of data reported in the literature for municipal waste incinerators was also carried out as part of the overall study program even though such sources were not directly tested. The results of the analysis of this data are:

1. Flue gas PCDD/PCDF emissions appear to be inversely related to furnace temperature, which itself is influenced directly by the presence of excess air and the heat content of the material combusted. Maximum emissions for a given site were found to be about 10 times higher when the feed was wet (relative to normal dry conditions).
2. Higher levels of dioxins and furans were found in the flue gases emitted from incinerators with flawed design and those which are poorly maintained.
3. In general, large amounts of PCDDs and PCDFs in flue gas are found for incinerators having large amounts of dioxins and furans in the flyash.
4. Levels of PCDDs and PCDFs in municipal incinerator flyash are a function of various design and operating conditions and not just the furnace temperature.
5. PCDD/PCDF emissions for European incinerators are generally higher than for American and Canadian facilities. There are no obvious reasons for this trend, although the differences may be due to differences in incinerator design and operation, incinerator age, as well as sampling and analytical methodologies.

The levels of dioxins and furans found in flyash samples of the Tier 4 test sites were also determined. The average values of the PCDD and PCDF contents of the ash samples and in the flue gas for the sites are compared in Table CIII. High levels in the flyash tend to correspond with high levels in the flue gas, however a direct relationship is not clearly evident.

By combining the emission data obtained from the Tier 4 test sites with that extracted from studies reported in the literature, a summary of PCDD/PCDF stack emissions for a variety of sources was compiled (see Table CIV).

The secondary copper smelter provided the highest emission of PCDDs and PCDFs while waste incinerators of all types were found to produce much lower levels. Variation among incinerators was widespread and although one cannot make any conclusions regarding the relative emissions of hazardous and municipal waste incinerators, it does appear that sewage sludge incinerators generally have the lowest emissions of the three. Kraft paper recovery boilers and coal-fired utility boilers all tend to emit relatively low levels of PCDDs and PCDFs.

Based on the results of the Tier 4 study and information extracted from the literature, the following conclusions were made:

1. PCDD and PCDF emissions appear to be higher for lower temperature combustion processes whose functions are to recover energy or other resources such as in the case of the secondary copper smelter.

2. Total organic halogen (TOX) levels showed the strongest association with the total level of PCDDs and PCDFs emitted whilesites with high percentages of plastics in the feed were found to yield high PCDD emissions in the Tier 4 sites studied.

3. Afterburners operating above 800 °C do not necessarily destroy all PCDDs and PCDFs since factors such as residence time and mixing are also significant.

4. Distribution profiles for the various PCDD and PCDF isomers were found to vary considerably amongst the sites tested in the Tier 4 program, however there were some similarities observed within sources of the same type. No universal pattern for combustion sources was found to exist.

Table LXXXVII: Summary of PCDD/PCDF Stack Emissions Data from the Literature

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/m³)		PCDD (ng/m³)		PCDF (ng/m³)		Reference/Comments
		Detected Range	Detection Limits	Detected Range	Detection Limits	Detected Range	Detection Limits	
Municipal Waste Incinerators								
- European (8)	FG^e	-	-	71-48,997 (8)	-	37-9,831 (8)	-	43, 87, 109
- U.S. and Canada (9)	FG	0.2-95 (6)	-	3.3-11,686 (9)	-	8.5-22,000 (9)	-	32, 49, 92, 101, 168, 174, 181, 196, 205
Boilers Cofiring Wastes								
- Commercial (3)	FG	-	-	1,400-17,000 (3)	NA^f (3)	170 (1)	NA (2)	81; - Boilers cofiring spiked waste oil. - PCDD refers to only TCDD and OCDD in this reference.
- Industrial (5)	FG	0.002 (1)	<0.002-1.5 (1)	0.64-76.4 (5)	<0.002-1,000 (4)	0.15-5.5 (3)	<0.002-1,000 (4)	40, 41; - Highest PCDD levels from 2 boilers firing creosote sludge. Creosote sludge feed for 1 boiler was contaminated with PCDD's.
- Utility (1)	FG	ND	<0.031-0.10 (1)	ND	<0.031-0.10 (1)	ND	<0.031-0.10 (1)	96; - PCB-spiked waste oil feed.
Wood Combustion								
- PCP-Treated Wood (2)	FG	-	-	1,520 (1)	<17ppb (1)	587 (1)	<17ppb (1)	220, 233; - The one unit with less than detectable emissions was designed to incinerate PCP-treated wood; the other unit was not. - Detection limits reported in terms of v/v.

(Continued)

Reproduced from best available copy.

Table LXXXVII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/m³) Detected Range	2378 TCDD (ng/m³) Detection Limits	PCDD (ng/m³) Detected Range	PCDD (ng/m³) Detection Limits	PCDF (ng/m³) Detected Range	PCDF (ng/m³) Detection Limits	Reference/Comments
Sewage Sludge Incinerators (2)	FG	-	-	812 (1)	NA (1)	1,374 (1)	NA (1)	24, 235: o In Ref. 235, results reported as "dioxins" and "furans" assumed to be PCDD/PCDF. o In Ref. 24, "fumes" were trapped with water condenser.
Hospital Incinerators (4)	FG	-	-	15-69 (4)	-	25-156 (4)	-	31a, 62a
Hazardous Waste Incinerators								
o Rotary Kiln (2)	FG	-	-	20.3-36.6 (2)	-	11.2-93.0 (2)	-	88, 153a: o Fuels were PCB's (88) and chlorophenolic wastes (153a).
Activated Carbon Regeneration								
o w/o Afterburner (1)	FG	0.1 (1)	-	0.18 (1)	-	0.3 (1)	-	13: o Fluidized bed combustion before installation of afterburner.
o w/ Afterburner (1)	FG	-	-	1.58 (1)	-	0.05 (1)	-	156: o Fluidized bed combustion after installation of afterburner. o PCDD means only H7CDD and OCDD homologs. o PCDF means only H6CDF, H7CDF, OCDF homologs.

(Continued)

Table LXXXVII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/m³) Detected Range	2378 TCDD (ng/m³) Detection Limits	PCDD (ng/m³) Detected Range	PCDD (ng/m³) Detection Limits	PCDF (ng/m³) Detected Range	PCDF (ng/m³) Detection Limits	Reference/Comments
Cement Kilns (3)	FG	-	-	1.35 (1)	<1 ng/ul (2)	0.74 (1)	<1 ng/ul (2)	20a, 20b, 184; o In one of four SASS trains, H7CDD and H7CDF homologs detected only (Ref. 184). o Detectable emissions occurred during upset combustion conditions. o Detection limits expressed in terms of ng/ul injected into GC-MS.
Lime Kilns (1)	FG	-	-	ND	<0.34-2.0 (1)	-	-	58a
Fossil Fuel Boilers								
o Coal-fired Utility (4)	FG	-	-	ND	<0.10-0.70 (4)	-	<0.10-0.70 (4)	94
o Pulverized Coal (1)	FG	ND	<4.2-7.9 (1)	-	-	-	<0.67-1.3 (1)	5; o 2378 TCDD/F scan only.
o Oil-fired Utility (1)	FG	ND	<4.2-7.9 (1)	-	-	-	<0.67-1.3 (1)	5; o 2378 TCDD/F scan only.

(Continued)

Table LXXXVII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/m^3) Detected Range	2378 TCDD (ng/m^3) Detection Limits	PCDD (ng/m^3) Detected Range	PCDD (ng/m^3) Detection Limits	PCDF (ng/m^3) Detected Range	PCDF (ng/m^3) Detection Limits	Reference/Comments
Incinerator Ships								
o M/T Vulcanus (1)	FG	-	-	ND	<0.0009-0.088 ng/ml (1)	-	-	1; o TCDD scan only. o Fuel was Herbicide Orange. o Detection limits expressed in terms of ng/ml injected into GC-MS.
o M/T Vulcanus (1)	FG	ND	NA (1)	ND	NA (1)	-	<0.3-3 (1)	2; o TCDD/TCDF scans only. o Feed samples were contaminated with PCDF's. o Feed was PCB's.

"—" means no data were available because analysis was not done or data were not reported.

[a]Detected Range is range of average levels detected. If only one value is shown it represents the average value of all tests for one unit. The number of sources having detectable emissions is shown in parentheses under the range values.

[b]Detection limits are shown when a source had less than detectable emissions. The number of sources having less than detectable emissions is shown in parentheses under the detection limits.

[c]The number in parentheses below each range represents the number of units having detectable or less than detectable emissions.

[d]ND = Not Detected

[e]FG = Flue Gas

[f]NA = Not Available

Reported PCDD/PCDF concentrations are reported "as measured."

Table LXXXVIII: Summary of Literature Data on PCDD and PCDF Contents of Combustion Ash a)b)c)

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/g)		PCDD (ng/g)		PCDF (ng/g)		Reference/Comments
		Detected Range	Detection Limits	Detected Range	Detection Limits	Detected Range	Detection Limits	
Hazardous Waste Incinerators								
o Rotary Kiln (1) w/o Supplemental Fuel	Part	1,870 (1)	-	321,570 (1)	-	-	-	62: o Results showed high by nonspecific analytical method used for one of three test runs. o No supplemental fuel fired in afterburner.
o Rotary Kiln (1) w/Supplemental Fuel	Part	ND*	<2-5 (1)	267 (1)	-	-	-	62: o Supplemental fuel fired in afterburner.
o Tar Burner (1)	Part	ND	<1.3-3 (1)	406 (1)	-	-	-	62
o Mobile Incinerator (1)	Ash	-	-	91.3 ng (1)	-	-	-	108: o OCDD homolog only. Suspected contaminant. Leakage of samples prevented concentration calculation.
o Rotary Kiln (3)	Part	-	-	ND	NA* (3)	ND	NA (2)	161

(Continued)

Table LXXXVIII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/g)		PCDD (ng/g)		PCDF (ng/g)		Reference/Comments
		Detected Range	Detection Limits	Detected Range	Detection Limits	Detected Range	Detection Limits	
PCB Transformer Fires (8)	Soot	59-600 (2)	-	324-19,400 (2)	<10-100 (2)	1,710-2,160,000 (4)	-	60, 99, 158: o 2 transformer fires with high PCDF levels had less than detectable levels of PCDD.
	Wipes	-	-	-	-	772-10,900 ng/m² (2)	-	76, 192: o Results reported in terms of surface area.
	Liquid	-	-	-	-	75,000 (1)	-	110: o Liquid from inside exploded capacitor.
	A.I.	-	-	5.2 (1)	-	41.4 (1)	-	218: o Only H7CDD and OCDD homologs detected.
Municipal Waste Incinerator								
o European (32)	FA	-	-	0.2-3537 (29)	NA (2)	1.93-1,770 (17)	-	12, 25, 26, 33, 43, 71, 116, 118, 143, 144, 178
o U.S. and Canada (21)	FA	5.2 (1)	-	6.2-2,300 (14)	-	10-3,100 (12)	-	47, 49, 69, 70, 71, 90, 92, 168, 181, 203, 222
o Japanese (2)	FA	-	-	2.4-4.8 (2)	-	-	-	71

(Continued)

Table LXXXVIII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/g) Detected Range	2378 TCDD (ng/g) Detection Limits	PCDD (ng/g) Detected Range	PCDD (ng/g) Detection Limits	PCDF (ng/g) Detected Range	PCDF (ng/g) Detection Limits	Reference/Comments
Fossil Fuel Combustion								
○ Natural Gas (1)	FA[1]	0.6 (1)	-	1,764 (1)	-	-	-	62; ○ HxCDD, H7CDD, and OCDD homologs only. Analyses by GC-EC
○ Coal and Oil (1)	[illegible]			68 (1)				62; ○ Feed may have had high chlorine content or contamination. ○ PSCDD not analyzed for.
○ Coal (13)	FA	-	-	ND	<0.0006-0.07 (13)	ND	<0.01-0.07 (1)	59, 94, 97, 125
Utilities Co-firing Wastes								
○ Commercial Boiler (1)	FA	-	-	911 (1)	-	1,777 (1)	-	81; ○ Co-firing used automobile oil spiked with organic compounds. ○ No TCDD's detected, only penta through octa homologs.
○ Industrial Boiler (1)	FA	-	-	600 (1)	-	300 (1)	-	33; ○ Co-firing used industrial oils.
Hospital Incinerator (1)	FA	-	-	259 (1)	-	265 (1)	-	31a

(continued)

Reproduced from best available copy.

Table LXXXVIII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/g) Detected Range	2378 TCDD (ng/g) Detection Limits	PCDD (ng/g) Detected Range	PCDD (ng/g) Detection Limits	PCDF (ng/g) Detected Range	PCDF (ng/g) Detection Limits	Reference/Comments
Wood Combustion								
o Residential Woodstoves (24)	Ash	0.001-0.20 (15)	<0.0009- 0.0014 (2)	0.007-210 (24)	-	-	-	54, 62, 105, 167; o Some fuel may have been contaminated.
Activated Carbon Regeneration								
o w/o Afterburner (1)	Part	25 (1)	-	48 (1)	-	103 (1)	-	13; o TCDD/TCDF scan only. o Fluidized bed combustion prior to installation of afterburner.
Automobile Emissions								
o Leaded gas (3)	Filter Extract	2.90 (3)	-	47.7 (3)	-	-	-	213; o One composite sample from 3 vehicles analyzed.
o Unleaded gas (10)	Filter Extract	1.4 (10)	-	37.4 (10)	-	-	-	213; o One composite sample from 10 vehicles analyzed.
o Diesel Truck (2)	Scraping	ND	<0.003 (2)	0.39-0.40 (2)	-	-	-	62
o Unleaded gas (2)	Scraping	ND	<0.0002 (2)	0.01-0.08 (2)	-	-	-	62
o Leaded gas (1)	Scraping	ND	<0.002 (1)	0.004 (1)	-	-	-	62
o Diesel Car (2)	Filter Extract	ND	<0.04 ng/sample (2)	ND	<0.04 ng/sample (2)	-	-	213 o TCDD scan only.

(continued)

Table LXXXVIII Continued

Source Category (Total # Tested)	Sample Type	2378 TCDD (ng/g) Detected Range	2378 TCDD (ng/g) Detection Limits	PCDD (ng/g) Detected Range	PCDD (ng/g) Detection Limits	PCDF (ng/g) Detected Range	PCDF (ng/g) Detection Limits	Reference/Comments
Wire Reclamation (1)	FA	-	-	0.41 (1)	-	11.6 (1)	-	103; o TCDD/TCDF scan only.
Cement Kiln (1)	Part	-	-	-	-	44.0 (1)	-	104; o One of four Method 5 filters contained PSCDF, HCDF, and H7CDF. o Detectable emissions occurred during upset operating conditions.
Lime Kiln (1)	Baghouse dust	-	-	ND	<0.005-0.25 (1)	-	-	58a
Sewage Sludge Incineration								
	FA	-	-	ND	NA (1)	-	-	24; o Fly ash collected by dust abatement.
	Ashes	-	-	ND	NA (1)	-	-	24

"-" means no data were available because analysis was not done.

FA = Fly Ash; Part. = Particulate phase of gaseous sample; Filter Extract = Particulate Filter Extract; Scraping = Muffler Exhaust Scraping

[a]Detected range is range of average levels detected. If only one value is shown it represents the average value of all tests for one unit. The number of sources having detectable emissions is shown in parentheses under the range values.

[b]Detection limits are shown when a source had less than detectable emissions. The number of sources having less than detectable emissions is shown in parentheses under the detection limits.

[c]The number in parentheses is number of units having detectable or less than detectable emissions.

[d]ND - Not Detected

[e]NA - Not Available

[f]Particulate material

Reproduced from best available copy.

Table LXXXIX: Preliminary Ranked Source Category List (October 1984)

Rank A Source Categories

Sewage Sludge Incinerators
Black Liquor Boilers

Rank B Source Categories

PCP Sludge Incinerators
Carbon Regeneration (Industrial)
Charcoal Manufacturing
Wire Reclamation Incinerators

Rank C Source Categories

Commercial Boilers Firing Fuels Contaminated with Chlorinated Organic Wastes
Woodstoves
Wood Boilers (Firing PCP-Treated Wood)
Mobile Sources
Small Spreader-Stoker Coal Boilers
Hazardous Waste Incinerators
Lime/Cement Kilns Cofired with Chlorinated Organic Wastes
Industrial Incinerators
Open Burning (Agricultural)
Apartment House Incinerators
Other Sources Recommended by State and Regional Offices (e.g., landfill flares, forest fires)

Rank D Source Categories

Municipal Solid Waste (MSW) Incineration
Industrial Boilers Cofiring Wastes

Rank A - Large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have the highest potential to emit TCDD.
Rank B - Small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have a high potential to emit TCDD.
Rank C - Source categories less likely to emit TCDD.
Rank D - Source categories that have already been tested three or more times.

SOURCE: Initial Literature Review

Table XC: Modification of Preliminary List

Source Category	Modification	Reason for Modification
PCP Sludge Incinerators	Rank B to Rank C	No longer practiced. This sludge is being incinerated in hazardous waste incinerators.
Industrial Incinerators	Rank C to Rank B	Many units operating in the U.S. Potential high level of chlorinated plastics in the feed.
Charcoal Manufacturing Operations	Rank B to Rank C	PCP-treated wood is not used to a large extent in this source category.
Wood-fired Boilers	Rank C to Rank B	Very large source cateogy. Some units burn wood stored in salt water (i.e., wood contains Cl^-).
Drum and Barrel Reclamation Furnaces	Add as Rank B	Over 100 facilities in U.S. Precursor levels may be high. Poor combustion conditions.
Secondary Metal Recovery Furnaces	Add as Rank B	Chlorinated plastics often present in the feed. PCDD detected in baghouse catch.
Hospital Waste Incinerators	Add as Rank C	Burning chlorinated plastics.

Table XCI: Final Ranked Source Category List

Rank A	Sewage Sludge Incinerators (3)
	Black Liquor Boilers (3)
Rank B	Industrial Incinerators (1)
	Wire Reclamation Incinerators (1)
	Carbon Regeneration Furnaces (1)
	Secondary Metal Blast Furnaces (1)
	Wood-Fired Boilers (1)
	Drum and Barrel Reclamation Furnaces (1)
Rank C	Mobile Sources[a] (1)
	Wood Stoves[a] (1)
	Spreader-Stoker Coal Fired Boilers
	Commercial Boilers Burning Chlorinated Organic Wastes
	Lime Kilns
	Cement Kilns
	Hazardous Waste Incinerators
	Hospital Waste Incinerators
	Apartment House Incinerators
	Charcoal Manufacturing Operations
	Open Burning
Rank D	Municipal Waste Incinerators
	Commercial Waste Boilers

(3) Indicates that the source category was tested three times under Tier 4.

(1) Indicates that the source category was tested once under Tier 4.

[a] Indicates that the source category was tested once under Tier 4 in conjunction with another test program.

Table XCII: Summary Description of the Tier 4 Test Sites

SEWAGE SLUDGE INCINERATORS

SSI-A	3.75 wet TPH Envirotech six-hearth multiple hearth incinerator controlled by a cyclone followed by a venturi/impingement tray scrubber. Average industrial contribution to treatment plant influent.
SSI-B	12.5 wet TPH Envirotech nine-hearth multiple hearth incinerator controlled by a cyclone followed by a waste heat boiler, a venturi scrubber and a subcooler. Average industrial contribution to treatment plant influent. Installed in 1983.
SSI-C	13.5 wet TPH Nichols twelve-hearth multiple hearth incinerator controlled by a 3 tray impingement scrubber. High industrial contribution to treatment plant influent. Installed in 1974.

BLACK LIQUOR BOILERS

BLB-A	900 TPD low odor B&W recovery boiler controlled by a wet bottom ESP. Average chloride content in black liquor. Installed in 1983.
BLB-B	800 TPD direct contact CE recovery boiler controlled by a dry bottom ESP. High chloride content in black liquor. Installed in 1962.
BLB-C	850 TPD low odor CE recovery boiler controlled by a dry bottom ESP. Average chloride content in black liquor. Installed in 1973.

WOOD COMBUSTION

Wood Fired Boiler WFB-A	100,000 lb/hr steam B&W Dutch oven boiler controlled by a baghouse. Salt-laden wood fired in the boiler. Installed in 1939.
Woodstove WS-A	Atlanta Stove Works free-standing non-catalytic woodstove. Oak and pine were burned during the tests.
Industrial Solid Waste Incinerator ISW-A	18 MMBtu/hr Kelley Model 2500 two-chamber controlled air incinerator with an afterburner. Incinerator feed contains polyvinyl chloride and pentachlorophenol-treated wood. Installed in 1981.

Table XCII Continued

SECONDARY METALS RECOVERY

Secondary Copper Blast Furnace MET-A	625 TPD (scrap input) rectangular shaft blast furnace with oxygen enrichment. Emissions controlled by afterburners and a baghouse system. Furnace feed contains plastic-bearing copper scrap.
Wire Reclamation Incinerator WRI-A	1200 lb/hr United Corporation Model G-466 batch feed wire reclamation incinerator controlled by a natural gas-fired afterburner. Incinerator feed consists of coated wire and/or drained transformer cores containing PCB's. Installed in 1978.

MISCELLANEOUS SOURCES

Drum and Barrel Reclamation Incinerator DBR-A (DBI-B)	150 drum/hr ECO Model 100 drum reclamation furnace controlled by a natural gas-fired afterburner. Combustible materials in feed include solvent residues and drum coatings. Drums originally contained lacquer, organic solvents, inks, enamel-type paints, etc. Installed in 1974.
Carbon Regeneration Furnace CRF-A	109,000 lb/day (bare carbon) multiple hearth furnace controlled by an afterburner, a sodium carbonate spray cooler, and a baghouse. Spent carbon feed was used for treatment of industrial wastewaters known to contain chlorinated organics. Furnace rebuilt in 1980.

Table XCIII: Mean Combustion Device Operating Parameters During the Test Runs

Source Category/ Test Site	Combustion Device Type	Process Feed Rate	Feed Characteristics	Auxiliary Fuel Firing Rate(s)	Process Temperatures Maximum	Process Temperatures Other	Oxygen (% O_2)^a
Sewage Sludge Incinerators							
SSI-A	Multiple (6) Hearth Incinerator	398 kg/hr (dry solids) Continuous Feed	21.1 wt.% dry solids 69.0% volatile solids	0.05 cmh No.2 fuel oil; 71 cmh digester gas	781°C (middle hearth)	424°C (top hearth)	11.9 (furnace outlet)
SSI-B	Multiple (8) Hearth Incinerator (1983)	2,600 kg/hr (dry solids) Continuous Feed	36.2 wt.% dry solids 74.7% volatile solids	None	849°C (middle hearth)	622°C (top hearth)	13.1 (furnace outlet)
SSI-C	Multiple Hearth Incinerator (12 hearths, 1974)	2,600 kg/hr (dry solids) Continuous Feed	20.3 wt.% dry solids 55.1 wt.% volatiles. (dry basis)	None	741°C (middle hearth)	444°C (top hearth)	13.2 (furnace outlet)
Black Liquor Boilers							
BLB-A	900 TPD B&W Low Odor Recovery Boiler (1983)	53,900 kg/hr (dry solids) Continuous Feed	65.0 wt.% solids	None	NA	--	3.6^a (economizer)
BLB-B	800 TPD CE Direct Contact Recovery Boiler (193)	56,800 kg/hr (dry solids) Continuous Feed	70.3 wt.% solids	None	NA	--	2.3^a (economizer)
BLB-C	850 TPD CE Low Odor Recovery Boiler (1973)	43,000 kg/hr (dry solids) Continuous Feed	63.1 wt.% solids	0.4 cmh Bunker C oil (Run 03 only)	NA	--	2.7^a (boiler outlet)
Wood Combustion							
WFB-A	100,000 lb/hr steam B&W Dutch Oven Boiler (1930)	5,900 kg/hr (dry wood) Semi-continuous Feed	52.7 wt.% dry solids 8,953 Btu/lb dry solids	None	899°C (secondary chamber)	--	13.0 (baghouse inlet)
ISW-A	10 MMBtu/hr (input) Kelly Model 2500 Controlled Air Incinerator (1981)	1,083 kg/hr (total feed) batch feed	5 waste materials in feed	0.03 cmh No. 2 oil (Runs 03, 04 only)	809°C (secondary chamber)	730°C (primary chamber)	11.3 (boiler outlet)

(Continued)

Table XCIII Continued

Source Category/ Test Site	Combustion Device Type	Process Feed Rate	Feed Characteristics	Auxiliary Fuel Firing Rate(s)	Process Temperatures Maximum	Process Temperatures Other	Oxygen (% O_2)[a]
Metals Recovery							
MET-A	Cupola Furnace	41,400 kg/hr batch feed	22.1 wt.% telephone scrap; 8.0 wt.% copper-bearing telephone scrap; 26.5 wt.% copper-bearing residues; 9.1 wt.% plant reverts; 34.3 wt.% slag reverts; all on coke-free basis	6,450 kg/hr Coke	877°C (cupola roof)	--	20.2 (stack breaching)
WRI-A (wire only)	545 kg/hr wire United Model G-466 Wire Reclamation Incinerator (1978)	361 kg/hr (total feed) batch feed	12.5 wt.% combustible materials; 100% from wire	36 cmh natural gas	1054°C (afterburner outlet)	566°C (primary chamber)	5.7 (afterburner outlet)
WRI-A (wire & transformers)	545 kg/hr wire United Model G-466 Wire Reclamation Incinerator (1978)	314 kg/hr (total feed) batch feed	19.8 wt.% combustible materials; 29% from wire, 71% from transformers	36 cmh natural gas	1000°C (afterburner outlet)	558°C (primary chamber)	7.4 (afterburner outlet)
Miscellaneous Sources							
DBR-A	4 MM Btu/hr (input) ECO Model 100 drum & barrel reclamation incinerator (1974)	120 drums/hr semi-continuous	Drums containing lacquer & organic solvents, inks, enamel-type paint and orange juice	195 cmh natural gas	827°C (afterburner outlet)	588°C (primary chamber)	13.5 (afterburner outlet)
CRF-A	2060 kg/hr spent carbon (bare carbon basis) multiple hearth furnace (7 hearths, 1980)	1080 kg/hr (bare carbon)	Spent activated carbon from industrial wastewater treatment	None	953°C (hearth)	(afterburner outlet temperatures are considered propietary by plant)	13.9 (afterburner outlet)

---

[a] Excess oxygen data for the black liquor boilers were obtained from plant-maintained in-situ oxygen monitors. Oxygen concentrations from this type of instrument are on a wet basis. Excess oxygen data for the other source categories were obtained by Radian using an extractive-type oxygen monitoring system. Oxygen concentrations from the extractive-type system are on a dry basis.

NA = [illegible], not available

Table XCIV: Average PCDD/PCDF Outlet Emission Concentrations from the Tier 4 Test Sites (Sites Ranked by Total PCDD Concentration)

Total PCDD Outlet Concentration Rank	Test Site	Source Type/Control Device Type	Average Outlet PCDD/PCDF Emission Concentrations (ng/dscm @ 3% O_2)			2378-TCDD Equivalent Emission Rate (g/yr)[b]
			2378-TCDD	Total PCDD	Total PCDF	
1	MET-A	Secondary Copper Cupola Furnace/AB, BH	232	11,900	60,700	829[c]
2	WRI-A	Wire Reclamation Incinerator/AB (wire and transformer feed)	0.2	705	666	0.012
3	ISW-A	Industrial Solid Waste Incinerator/AB	4.5	625	2,390	0.74
4	WFB-A	Salt Laden Wood Fired Boiler/BH	0.1	195	83.2	0.559
5	WRI-A	Wire Reclamation Incinerator/AB (wire only feed)	0.1	173	305	0.012
6	SSI-C	Sewage Sludge Incinerator/SCR	0.1	52.7	446	2.23
7	SSI-A	Sewage Sludge Incinerator/SCR	0.05	19.6	43.5	0.016
8	DBR-A	Drum and Barrel Incinerator/AB	0.05	5.0	27.0	0.009
9	CRF-A	Carbon Regeneration Furnace/AB,SD,BH	ND (0.2)	3.7	3.3	0.023
10	BLB-C	Black Liquor Boiler/ESP	ND (0.01)	2.9	2.1	0.253
11	SSI-B	Sewage Sludge Incinerator/SCR	ND (0.1)	1.6	27.6	0.044
12	BLB-B	Black Liquor Boiler/ESP	ND (0.03)	1.2	0.7	0.030
13	BLB-A	Black Liquor Boiler/ESP	ND (0.04)	0.8	0.6	0.027
14	WS-A	Woodstove/Uncontrolled	NR	NR	NR	--

[a] Analytical data for Sites MET-A and WRI-A did not satisfy the Tier 4 QA/QC criteria for all test runs. Values shown in this table correspond to average for all test runs. Values for individual runs are contained in Appendix A.

[b] 8160 operating hours per year.

[c] Based on 2378-TCDD concentration of 170 ng/dscm @ 3% O_2.

ND = not detected (average detection limit in parenthesis)
NR = No valid analytical data were reported
AB = afterburner

BH = baghouse
SCR = scrubber
SD = spray dryer
ESP = electrostatic precipitator

Reproduced from best available copy.

Table XCV: Toxic Equivalency Factors Used in Estimating 2,3,7,8-TCDD Equivalents [a]

Compound(s)	Toxic Equivalency Factor
2378-TCDD	1.0
Other TCDDs*	0.01
Penta-CDDs	0.5
Hexa-CDDs	0.04
Hepta-CDDs	0.001
Octa-CDDs	0.000
2378-TCDF	0.1
Other TCDFs*	0.001
Penta-CDFs	0.1
Hexa-CDFs	0.01
Hepta-CDFs	0.001
Octa-CDFs	0.000

*In situations where 2378-TCDD or TCDF were not chemically analyzed in the sample, total TCDDs and TCDFs will have a relative potency factor of 1.0 and 0.1, respectively.

[a] Reference: U.S. Environmental Protection Agency. Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated-Dibenzodioxins and -Dibenzofurans (CDD and CDF). The Risk Assessment Forum, Washington, D.C. EPA 625/3-87-012.

Table XCVI: Average Control Device Inlet PCDD/PCDF Emission Concentrations From the Tier 4 Test Sites (Sites Ranked by Outlet Total PCDD Concentration)

Inlet Total PCDD Concentration Rank	Test Site	Source Type/Control Device Type	Average Inlet PCDD/PCDF Concentrations (ng/dscm @ 3% O_2)		
			2378-TCDD	Total PCDD	Total PCDF
1	MET-A	Secondary Copper Cupola Furnace/AB, BH	NS	NS	NS
2	WRI-A	Wire Reclamation Incinerator/AB (wire and transformer feed)	NS	NS	NS
3	ISW-A	Industrial Solid Waste Incinerator/AB	NS	NS	NS
4	WFB-A	Salt-Laden Wood Fired Boiler/BH	0.9	102	156
5	WRI-A	Wire Reclamation Incinerator/AB (wire-only feed)	NS	NS	NS
6	SSI-C	Sewage Sludge Incinerator/SCR	NR	114	507
7	SSI-A	Sewage Sludge Incinerator/SCR	NR	NR	NR
8	DBR-A	Drum and Barrel Incinerator/AB	16.4	687	2,170
9	CRF-A	Carbon Regeneration Furnace/AB,SD,BH	0.09	20.8	70.1
10	BLB-C	Black Liquor Boiler/ESP	NR	9.0	15.1
11	SSI-B	Sewage Sludge Incinerator/SCR	NS	NS	NS
12	BLB-B	Black Liquor Boiler/ESP	ND (0.05)	17.1	1.1
13	BLB-A	Black Liquor Boiler/ESP	ND (0.04)	1.8	1.5
14	WS-A	Woodstove/Uncontrolled	NR	NR	NR

ND = not detected (average detection limits in parenthesis)
NR = no valid analytical data were reported
AB = afterburner
NS = not sampled

BH = baghouse
SCR = scrubber
SD = spray dryer
ESP = electrostatic precipitator

Table XCVII: Average Outlet PCDD/PCDF Mass Emission Rates for the Tier 4 Test Sites (Sites Ranked by Total PCDD Mass Emission Rates)

Outlet Total PCDD Mass Emission Rate Rank	Test Site	Source Type/Control Device Type	Average Mass Emission Rates (ug/hr)		
			2378-TCDD	Total PCDD	Total PCDF
1	MET-A	Secondary Copper Cupola Furnace/AB, BH	5.360	283.000	1.420.000
2	WFB-A	Salt-Laden Wood Fired Boiler/BH	5.8	4.190	1.800
3	ISW-A	Industrial Solid Waste Incinerator/AB	13.5	1.810	6.780
4	SSI-C	Sewage Sludge Incinerator/SCR	2.1	780	6.570
5	BLB-C	Black Liquor Boiler/ESP	ND (1.6)	667	330
6	WRI-A	Wire Reclamation Incinerator/AB (wire and transformer feed)	0.1	522	626
7	BLB-B	Black Liquor Boiler/ESP	ND (5.1)	230	214
8	BLB-A	Black Liquor Boiler/ESP	ND (7.2)	149	114
9	WRI-A	Wire Reclamation Incinerator/AB (wire-only feed)	0.1	113	205
10	SSI-A	Sewage Sludge Incinerator/SCR	0.1	40.5	90.4
11	CRF-A	Carbon Regeneration Furnace/AB,SD,BH	ND (2.0)	31.6	28.9
12	DBR-A	Drum and Barrel Incinerator/AB	0.3	23.8	129
13	SSI-B	Sewage Sludge Incinerator/SCR	ND (1.0)	11.6	194
14	WS-A	Woodstove/Uncontrolled	NR	NR	NR

[a] Analytical data for Sites MET-A and WRI-A did not satisfy the Tier 4 QA/QC criteria for all test runs. Values shown correspond to averages for all test runs. Values for individual runs are contained in the corresponding site-specific test reports.

ND = not detected (average detection limit in parenthesis)
AB = afterburner
BH = baghouse
NR = no valid analytical data were reported
SCR = scrubber
SD = spray dryer
ESP = electrostatic precipitator

Reproduced from best available copy

Table XCVIII: Average Control Device Inlet PCDD/PCDF Mass Flow Rates for the Tier 4 Test Sites (Sites Ranked by Outlet Total PCDD Mass Emission Rates)

Outlet Total PCDD Mass Emission Rate Rank	Test Site	Source Type/Control Device Type	Average Inlet PCDD/PCDF Mass Flow Rates (ug/hr) 2378-TCDD	Total PCDD	Total PCDF
1	MET-A	Secondary Copper Cupola Furnace/AB, BH	NS	NS	NS
2	WFB-A	Salt-Laden Wood Fired Boiler/BH	24.0	2,640	4,380
3	ISW-A	Industrial Solid Waste Incinerator/AB	NS	NS	NS
4	SSI-C	Sewage Sludge Incinerator/SCR	NR	1,790	7,900
5	BLB-C	Black Liquor Boiler/ESP	NR	1,060	1,810
6	WRI-A	Wire Reclamation Incinerator/AB (wire and transformer feed)	NS	NS	NS
7	BLB-B	Black Liquor Boiler/ESP	ND (9.4)	3,380	383
8	BLB-A	Black Liquor Boiler/ESP	ND (8.0)	339	283
9	WRI-A	Wire Reclamation Incinerator/AB (wire-only feed)	NS	NS	NS
10	SSI-A	Sewage Sludge Incinerator/SCR	NR	NR	NR
11	CRF-A	Carbon Regeneration Furnace/AB, SD, BH	1.0	310	754
12	DBR-A	Drum and Barrel Incinerator/AB	24.2	1,050	3,110
13	SSI-B	Sewage Sludge Incinerator/SCR	NS	NS	NS
14	WS-A	Woodstove/Uncontrolled	NR	NR	NR

NR = no valid analytical data were reported
ND = not detected (average detection limit in parenthesis)
NS = not sampled
SD = spray dryer

AB = afterburner
BH = baghouse
SCR = scrubber
ESP = electrostatic precipitator

Table XCIX: Average Outlet Scaled PCDD/PCDF Mass Emissions for the Tier 4 Test Sites

Test Site	Basis of Feed Rate Scaling Factor[a]	Average Outlet Scaled Mass Emissions (ug/kg)		
		2378-TCDD	Total PCDD	Total PCDF
Sewage Sludge Incinerators				
SSI-A	Dry Sludge Feed Rate	2.2×10^{-4}	1.0×10^{-1}	2.3×10^{-1}
SSI-B	Dry Sludge Feed Rate	ND(3.4×10^{-4})	4.8×10^{-3}	8.3×10^{-2}
SSI-C	Dry Sludge Feed Rate	9.4×10^{-4}	3.6×10^{-1}	3.0×10^{0}
Black Liquor Boilers				
BLB-A	Dry Solids Feed Rate	ND(1.3×10^{-4})	2.8×10^{-3}	2.1×10^{-3}
BLB-B	Dry Solids Feed Rate	ND(8.9×10^{-5})	4.1×10^{-3}	2.4×10^{-3}
BLB-C	Dry Solids Feed Rate	ND(3.8×10^{-5})	1.6×10^{-2}	7.9×10^{-3}
Wood Combustion				
WFB-A	Wood Feed Rate (wet)	9.9×10^{-4}	7.1×10^{-1}	3.1×10^{-1}
WS-A	Wood Feed Rate (wet)	NR	NR	NR
TSW-A	Total Solids Feed Rate	1.3×10^{-2}	1.7×10^{0}	6.3×10^{0}
Metals Recovery				
MET-A	Copper-Bearing Feed Rate	1.3×10^{-1}	6.4×10^{0}	$3.3 \times 10^{+1}$
WRI-A (wire only)	Total Solids Feed Rate	2.8×10^{-4}	3.6×10^{-1}	6.3×10^{-1}
WRI-A (wire & transformers)	Total Solids Feed Rate	3.7×10^{-4}	1.4×10^{0}	1.8×10^{0}
Miscellaneous Sources				
DBR-A	Drum Feed Rate[b]	2.1×10^{-3}	2.0×10^{-1}	1.1×10^{0}
CRF-A	Spent Carbon Feed Rate	ND(2.1×10^{-3}	3.1×10^{-2}	2.7×10^{-2}

ND = not detected (average detection limit in parenthesis)

[a] All scaled mass emissions calculated using feed rates expressed in units of kg/hr of the specified feed material except for Site DBR-A, for which the feed rate was expressed in units of number of drums processed per hour.

[b] Scaled mass emissions for Site DBR-A are based on the number of drums processed per hour.

Table C: Average Control Device Inlet Scaled PCDD/PCDF Mass Flow for the Tier 4 Test Sites

Test Site	Basis of Feed Rate Scaling Factor[a]	Average Scaled Inlet PCDD/PCDF Mass Flow (ug/kg)		
		2378-TCDD	Total PCDD	Total PCDF
Sewage Sludge Incinerators				
SSI-A	Dry Sludge Feed Rate	NR	NR	NR
SSI-B	Dry Sludge Feed Rate	NS	NS	NS
SSI-C	Dry Sludge Feed Rate	NR	8.2×10^{-1}	3.6×10^{0}
Black Liquor Boilers				
BLB-A	Dry Solids Feed Rate	ND(1.4×10^{-4})	6.3×10^{-3}	5.3×10^{-3}
BLB-B	Dry Solids Feed Rate	ND(1.7×10^{-4})	5.9×10^{-2}	3.7×10^{-3}
BLB-C	Dry Solids Feed Rate	NR	2.5×10^{-2}	4.1×10^{-2}
Wood Combustion				
WFB-A	Wood Feed Rate (wet)	4.1×10^{-3}	4.9×10^{-1}	7.5×10^{-1}
WS-A	Wood Feed Rate (wet)	NR	NR	NR
ISW-A	Total Solids Feed Rate	NS	NS	NS
Metals Recovery				
MET-A	Copper-Bearing Feed Rate	NS	NS	NS
WRI-A (wire only)	Total Solids Feed Rate	NS	NS	NS
WRI-A (wire & transformers)	Total Solids Feed Rate	NS	NS	NS
Miscellaneous Sources				
DBR-A	Drum Feed Rate[b]	2.1×10^{-1}	8.8×10^{0}	2.6×10^{1}
CRF-A	Spent Carbon Feed Rate	8.9×10^{-4}	3.0×10^{-1}	7.0×10^{-1}

[a] All emission factors calculated using feed rates expressed in units of kg/hr of the specified feed material except for Site DBH-A, for which the feed rate was expressed in units of number of drums processed per hour.

[b] Emission factors for Site DBR-A are based on the number of drums processed per hour.

NS = uncontrolled emissions not sampled; NR = analytical data not reported; NA = feed rate data not available

Table CI: Dioxin/Furan Precursor Data Summary

		GC/MS Precursor Analysis			Hall Detector Analysis	Ion Chromatography Analysis
		Base/Neutrals Fraction		Acids Fraction		
Source Category/ Test Site	Sample Type	Chlorobenzene (ug/g)	Chlorinated Biphenyls (ug/g)	Chlorophenols (ug/g)	Total TOX (ug/g)	Total Cl (ug/g)
Sewage Sludge Incinerators						
SSI-A	Sludge Feed	ND - 0.01	ND	ND	NA	600
	Fuel Oil	NA	NA	NA	ND	35
SSI-B	Sludge Feed	0.01 - 0.04	ND	ND	NA	240
SSI-C	Sludge Feed	ND - 0.03	ND	ND	ND	300
Black Liquor Boilers						
BLB-A	Black Liquor	ND	ND	ND - 0.014	NA	900
BLB-B	Black Liquor	ND	ND	ND - Trace	ND	5,280
BLB-C	Black Liquor	ND	ND	ND - 0.01	NA	3,350
	Fuel Oil	NA	NA	NA	ND	170
Wood Combustion						
WFB-A	Wood Feed	ND	ND	ND	ND	1,880
WS-A	Oak	ND	ND	ND	NA	125
	Pine	ND	ND	ND	NA	49

(Continued)

Table CI Continued

		GC/MS Precursor Analysis			Hall Detector Analysis	Ion Chromatography Analysis
		Base/Neutrals Fraction		Acids Fraction		
Source Category/ Test Site	Sample Type	Chlorobenzene (ug/g)	Chlorinated Biphenyls (ug/g)	Chlorophenols (ug/g)	Total TOX (ug/g)	Total Cl (ug/g)
Wood Combustion (Continued)						
ISW-A	Cardboard, paper, and wood	ND	ND	0.04 - 0.11	12.7^a	9668
	Wood and plastic parts	ND	ND - 0.05	5.7 - 19.7		NA
	Oil-based paint sludge	ND	ND	ND - 0.03	NA	NA
	Latex paint sludge	ND	ND - Trace	Trace - 0.03	NA	NA
	Fuel oil	ND	ND	ND	NQ - 22.2	30
Metals Recovery						
MET-A	Metallurgical coke	ND	ND	ND	NA	NA
	Miscellaneous telephone parts and wire	ND	0.004	ND	NA	NA
	Circuit boards	ND	ND	ND	4.303^b	NA
	Electrical switching gear	ND	0.26	ND		NA

(Continued)

Reproduced from best available copy

Table CI Continued

		GC/MS Precursor Analysis			Hall Detector Analysis	Ion Chromatography Analysis
		Base/Neutrals Fraction		Acids Fraction		
Source Category/ Test Site	Sample Type	Chlorobenzene (ug/g)	Chlorinated Biphenyls (ug/g)	Chlorophenols (ug/g)	Total TOX (ug/g)	Total Cl (ug/g)
Metals Recovery (Continued)						
WRI-A	Wire coating and insulation	ND	ND	Trace	201	NA
	Transformer core parts (cardboard, wood, paper)	ND[c]	ND[c]	0.2	20.9 - 24.1	270
Miscellaneous Sources						
DBR-A	Drum residue (solvent)	ND - 68.6	ND	ND	802	4,700
	Drum coating	ND - 0.22	ND	ND	NA	50
CRF-A	Spent carbon	0.16 - 6.63	ND	ND	154	6,400

ND = not detected

NA = not analyzed

[a] TOX analysis was performed on a composite of the cardboard, paper, and wood samples and the wood and plastic parts samples.

[b] TOX analysis was performed on a composite of the circuit board samples and the electrical switching gear samples.

[c] The base/neutrals fraction of this sample could not be analyzed successfully by GC/MS. The sample was analyzed for Total Organic Halogen and a chromatographic profile was obtained by gas chromatography using electron capture detection.

Table CII: Tier 4 Surrogate Measurements for Factors Affecting Dioxin Emissions

Factors Affecting Dioxin Emissions	Variable or Surrogate Variable Measured in the Tier 4 Program
PCDD in feed	None (some feed samples archived for potential PCDD analysis)
Precursors in feed	Chlorobenzenes, chlorophenols, PCB's and TOX in feed
Chlorine in feed	Chlorine in feed and HCl emissions
Combustion temperature	Combustion chamber temperature or flue gas temperature
Residence time	Not measured, no surrogate
Oxygen availability	O_2 content of stack gas, CO emissions, THC emissions
Feed processing	Broad characterizations of feed types, moisture content of feeds (if appropriate), feed rate
Supplemental fuel	Fuel flow and heat input recorded, if available

NOTE: TOX = total organic halogen content of feed
THC = total hydrocarbon concentration in flue gas

Table CIII: Comparison of Tier 4 Ash and Flue Gas Data

Source Category	Site	Ash Sample Type	Average PCDD/PCDF Content: Ash (ppt): 2378-TCDD	Ash (ppt): Total PCDD	Ash (ppt): Total PCDF	Flue Gas (ng/dscm @ 3% O_2)[a]: 2378-TCDD	Flue Gas: Total PCDD	Flue Gas: Total PCDF
Sewage Sludge Incinerators	SSI-A	Bottom Ash	ND	ND	ND	0.05	19.6	34.5
	SSI-C	Bottom Ash	ND	20	70	0.1	52.7	446
		Scrubber water filterable solids (ng/l)	ND	0.7	13			
		Scrubber water filtrate (ppt)	ND	0.3	4.0			
		(ng/l scrubber water)	ND	2×10^{-5}	3×10^{-4}			
	SSI-B	Bottom Ash	ND	10	50	ND	1.6	27.6
Black Liquor[b] Boilers	BLB-C	ESP Ash	ND	20	20	ND	2.9	2.1
Wood Combustion	ISW-A	Bottom Ash	140	138,200	7,400	4.5	625	2390
	WFB-A	Bottom Ash - Primary	NR	150	ND			
		Bottom Ash - Secondary	NR	100	ND			
		Baghouse Dust	100	1,143,600	315,600	0.3	195	83.2
Metals	WRI-A	Bottom Ash - Primary						
		Wire Only	20	240,000	730,000	0.1	173	305
		Wire & Transformer	ND	19,500	82,000	0.1	705	866
		Settling Chamber						
		Wire Only	20	521,000	2,610,300			
		Wire & Transformer	6	231,000	657,600			
	MEI-A	Baghouse Dust	150	106,600	571,700	232	11,900	60,700
	DBR-A[c]	Bottom Ash	0.03	17	16	16	688	2,165
Miscellaneous	CRF-A	Baghouse Ash	ND	110	50	ND	3.7	3.3

[a] Flue gas concentration shown for outlet location.

[b] At Site BLB-A, particulates were controlled with wet bottom ESP's, therefore samples were not collected. At Site BLB-B, particulates were controlled with a dry bottom ESP, but the sampling location was inaccessible.

[c] For Site DBR-A, contamination prevented meaningful and valid results.

DBR = Drum and barrel incinerator
SSI = Sewage sludge incinerator
BLB = Black liquor boiler
ISW = Industrial solid waste incinerator
WFB = Wood-fired boiler
WRI = Wire reclamation incinerator
CRF = Carbon regeneration furnace

Table CIV: Summary of PCDD/PCDF Stack Emissions By Source Category

	Source Category	Number of Units[a]		Range of PCDD Emissions [ng/m³]	Range of PCDF Emissions [ng/m³]
		Tier 4	Lit.		
1.	Municipal Waste Incinerators				
	European	0	8	71-48,997	37-9,831
	U.S. and Canada	0	10	3.3-11.686	8.5-22,000
2.	Boilers Cofiring Waste				
	Commercial	0	3	1,400-17,000	170
	Industrial	0	5	<0.002[b]-76.4	<0.002-5.5
3.	Secondary Copper Cupola Furnace	1	0	11,900	60,700
4.	Wood Combustion				
	PCP-Treated Wood	0	2	<17[c]-1.520	<17[c]-587
	Salt-Laden Wood-Fired Boiler	1	0	195	83.2
5.	Sewage Sludge Incinerators	3	2	ND[d]-812	ND[d]-1.374
6.	Wire Reclamation Incinerator (wire and transformer feed)	1	0	704	866
7.	Industrial Solid Waste Incinerator	1	0	625	2.390
8.	Wire Reclamation Incinerator (wire-only feed)	1	0	173	305
9.	Hospital Incinerators	0	4	15-69	25-156
10.	Hazardous Waste Incinerators				
	Rotary Kiln	0	2	7.7-8.6	11.2-19
11.	Drum & Barrel Reclamation Incinerator	1	0	5	27
12.	Carbon Regeneration Furnace				
	without Afterburner	0	1	0.18	0.3
	with Afterburner	1	1	1.6-3.7	0.05-3.3
13.	Black Liquor Boiler	3	0	0.8-2.9	0.6-2.1
14.	Cement Kilns	0	3	<1[e]-1.35	<1[e]-0.74
15.	Lime Kilns	0	1	<0.34-<2.0	----
16.	Utility Boiler				
	Co-firing Waste	0	1	<0.031-<0.10	<0.31-<0.10
17.	Fossil Fuel Combustion				
	Coal-Fired Utility	0	4	<0.10-<0.70	<0.10-<0.70
	Pulverized Coal	0	1	<4.2-<7.9[f]	<0.67-<1.3[f]
	Oil-Fired Utility	0	1	<4.2-<7.9[f]	<0.67-<1.3[f]
18.	Incinerator Ship	0	1	<0.0009-<0.086[g]	<0.3-<3.0

SEWAGE SLUDGE INCINERATORS INLET

Site SSI - A

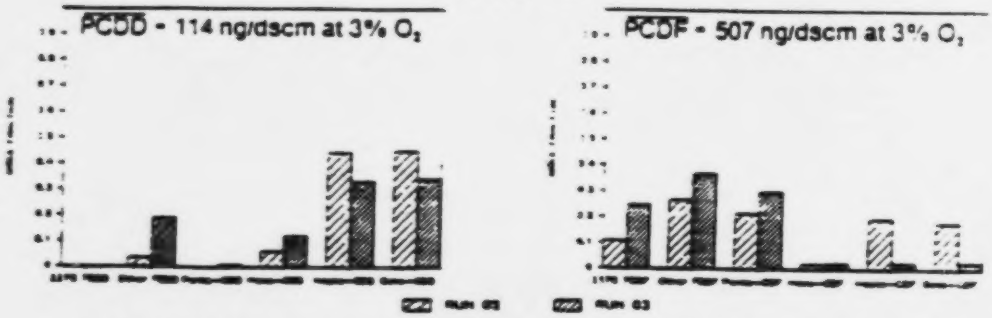
Analytical Data were not Reported by Troika for the Inlet MM5 Samples taken at Site SSI - A due to Unacceptable Surrogate Recovery Results

Site SSI - B

Uncontrolled Emissions from Site SSI - B were not Sampled

DIOXINS **FURANS**

Site SSI - C

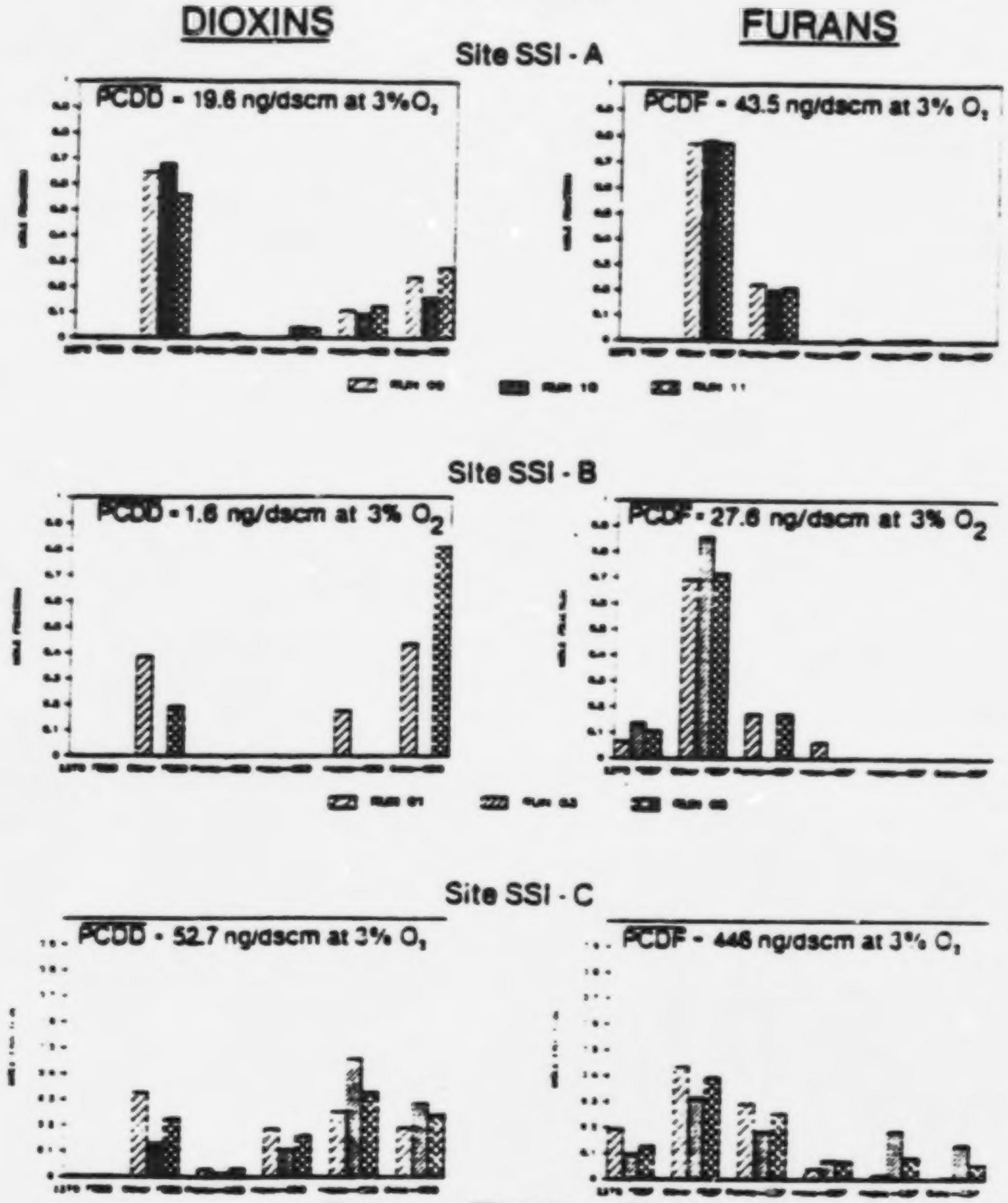


Dioxin/Furan Homologue Distributions of Uncontrolled Emissions from Sewage Sludge Incinerators (Sites SSI - A, SSI - B, SSI - C)

Figure 43: Sewage Sludge Incinerators Inlet

Reproduced from best available copy.

SEWAGE SLUDGE INCINERATORS OUTLET



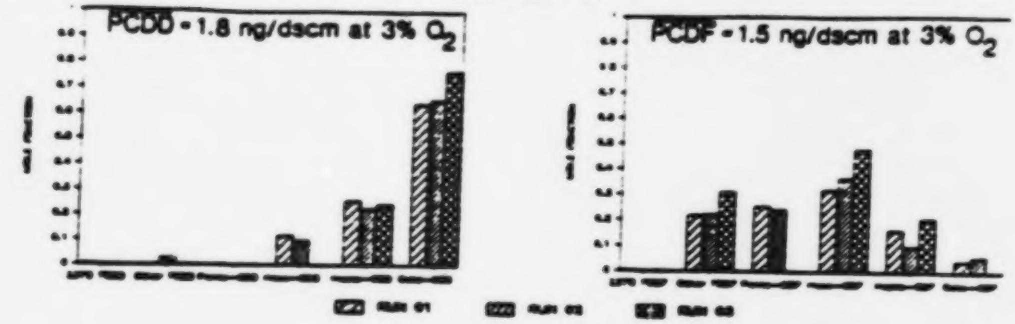
Dioxin/Furan Homologue Distibutions of Controlled Emissions from Sewage Sludge Incinerators (Sites SSI - A, SSI - B, SSI - C)

Figure 44: Sewage Sludge Incinerators Outlet

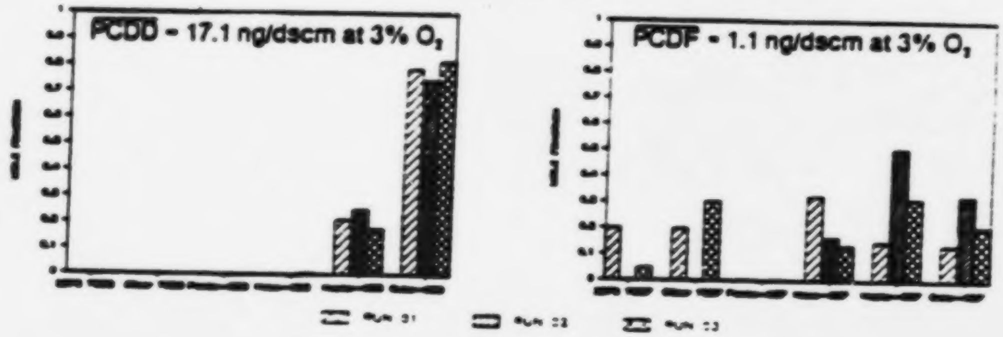
BLACK LIQUOR BOILERS/INLET

DIOXINS **FURANS**

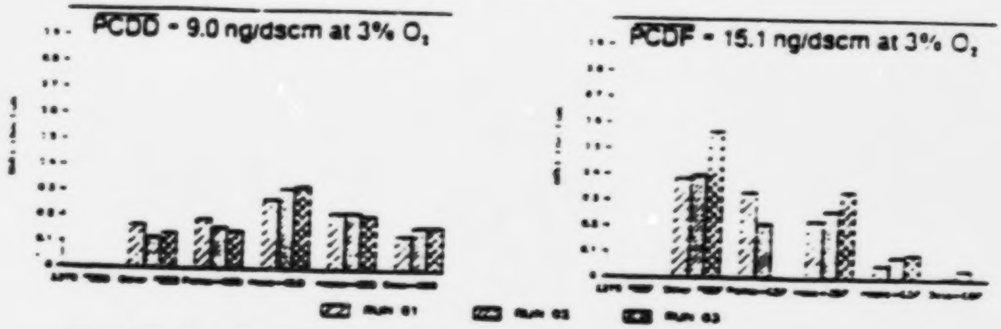
Site BLB - A



Site BLB - B



Site BLB - C



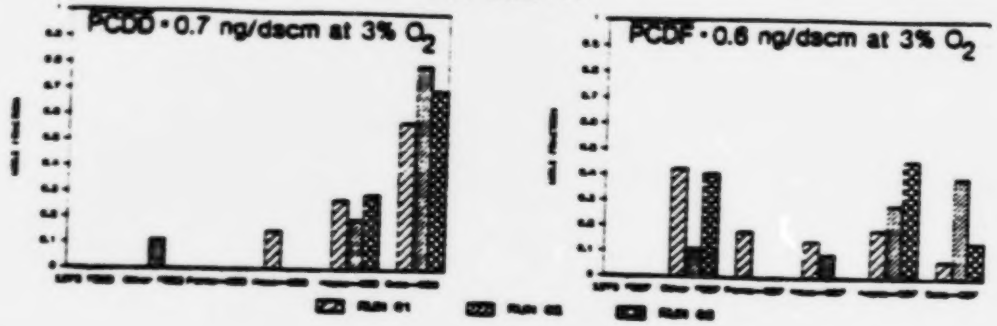
Dioxin/Furan Homologue Distributions of Uncontrolled Emissions from Black Liquor Boilers (Sites BLB - A, BLB - B, BLB - C)

Figure 45: Black Liquor Boilers/Inlet

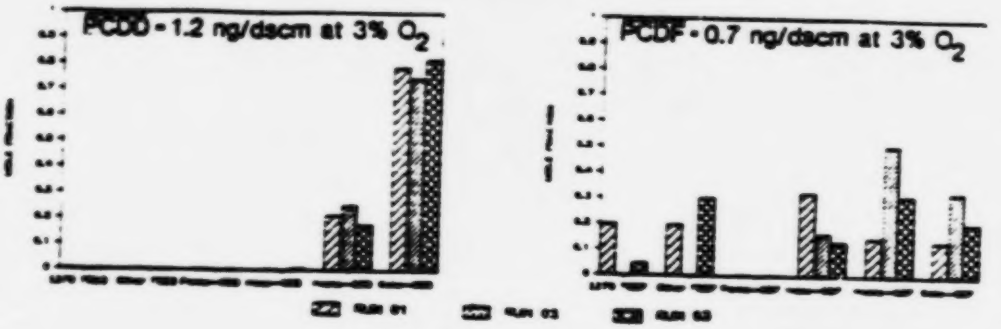
BLACK LIQUOR BOILERS/OUTLET

DIOXINS **FURANS**

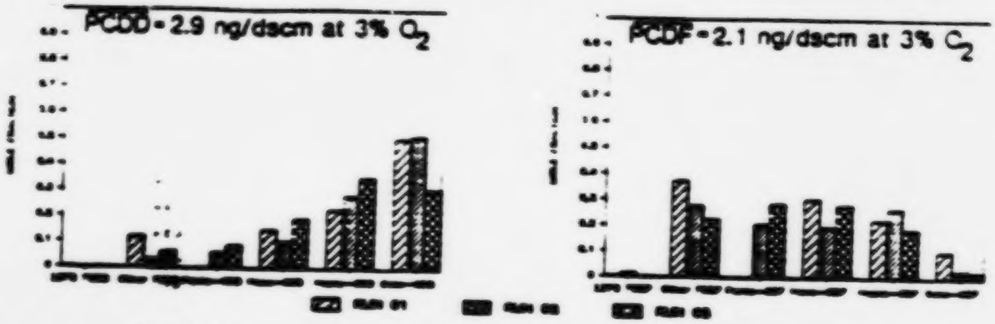
Site BLB - A



Site BLB - B



Site BLB - C



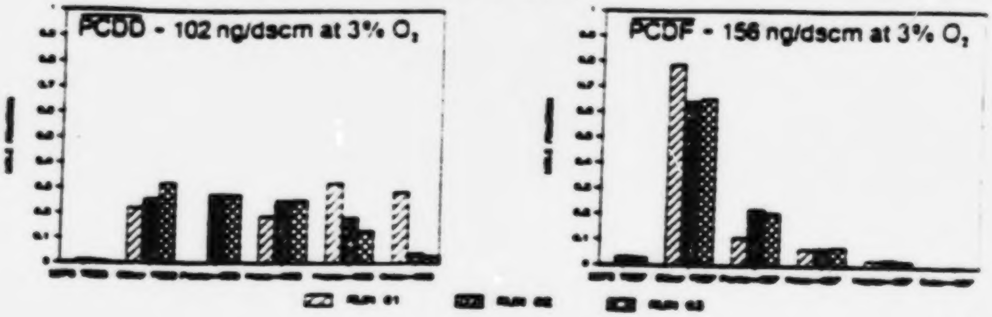
Dioxin/Furan Homologue Distributions of Controlled Emissions
from Black Liquor Boilers
(Sites BLB - A, BLB - B, BLB - C)

Figure 46: Black Liquor Boilers/Outlet

Reproduced from
best available copy.

WOOD COMBUSTION/INLET

DIOXINS Site WFB - A **FURANS**



Site ISW - A

Uncontrolled Emissions from Site ISW - A were not Sampled

Site WS - A

Analytical Data were not Reported by Troika for MMS Samples taken at Site WS - A due to Unacceptable Surrogate Recovery Results

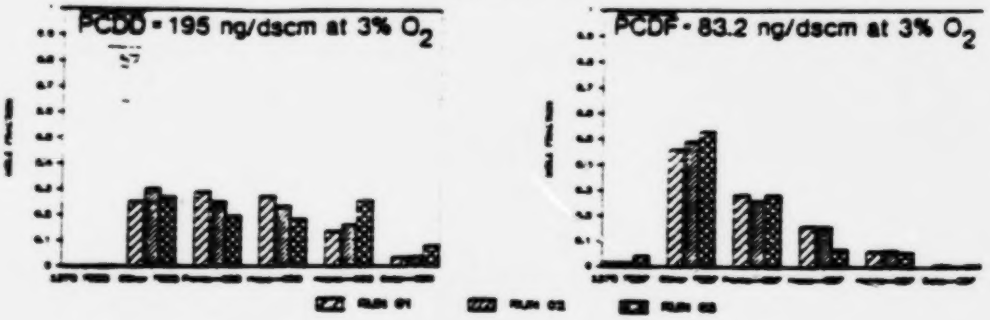
Dioxin/Furan Homologue Distributions of Uncontrolled Emissions from Wood Combustion Processes (Sites WFB - A, ISW - A, WS - A)

Figure 47: Wood Combustion/Inlet

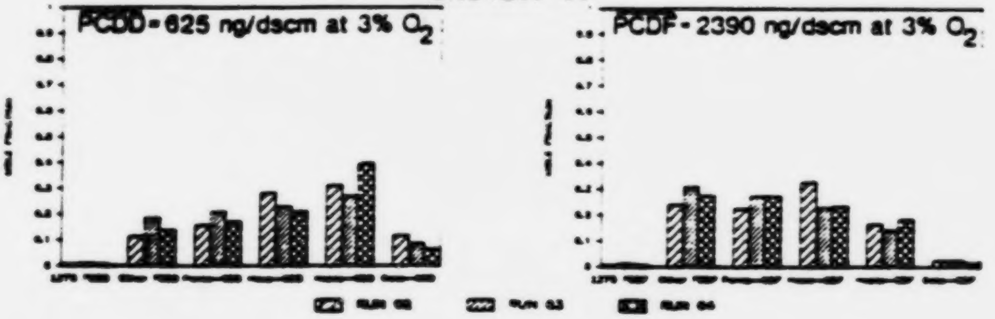
WOOD COMBUSTION/OUTLET

DIOXINS **FURANS**

Site WFB - A



Site ISW - A



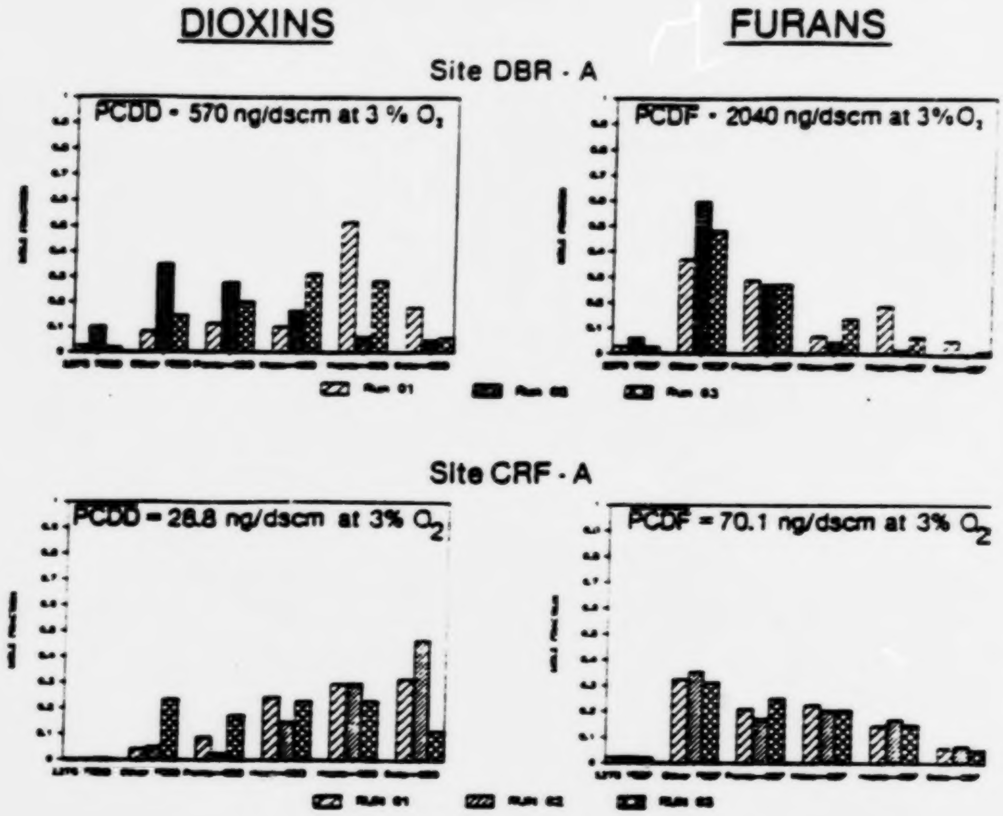
Site WS - A

Analytical Data were not Reported by Troika for MMS Samples taken at Site WS - A due to Unacceptable Surrogate Recovery Results

Dioxin/Furan Homologue Distributions of Controlled Emissions from Wood Combustion Processes (Sites WFB - A, ISW - A, WS - A)

Figure 48: Wood Combustion/Outlet

MISCELLANEOUS COMBUSTION SOURCES/INLET



Dioxin/Furan Homologue Distributions of Uncontrolled Emissions from Miscellaneous Combustion Sources (Sites DBR - A, CRF - A)

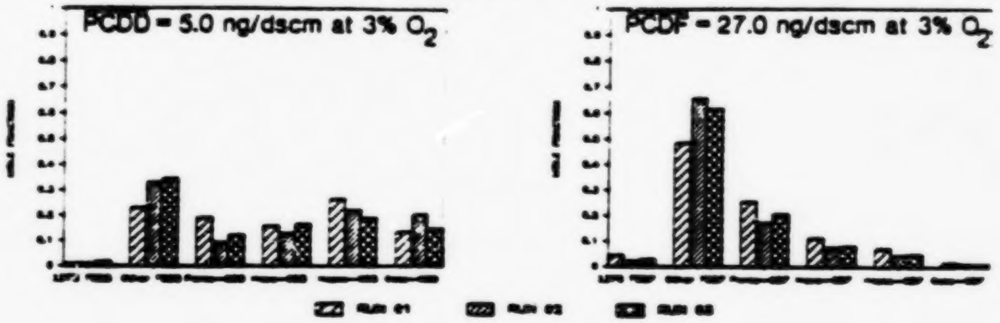
Figure 49: Miscellaneous Combustion Sources/Inlet

Reproduced from best available copy.

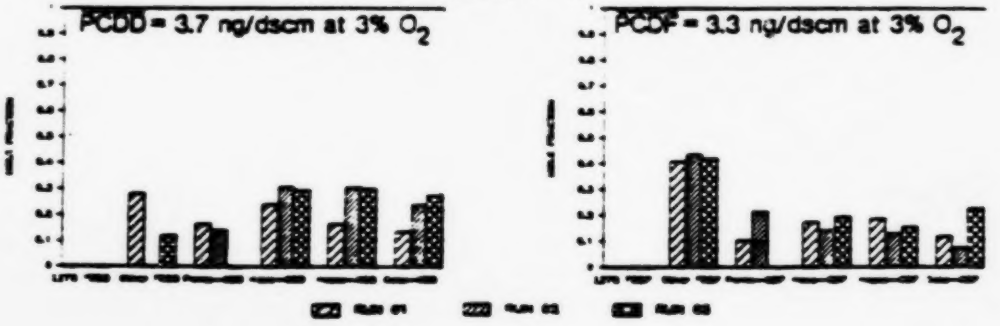
MISCELLANEOUS COMBUSTION SOURCES/OUTLET

DIOXINS **FURANS**

Site DBR - A



Site CRF - A



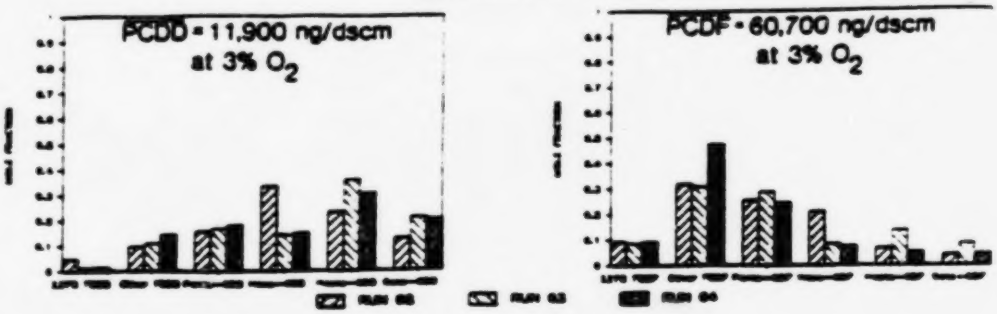
Dioxin/Furan Homologue Distributions of Controlled Emissions from Miscellaneous Combustion Sources (Sites DBR - A, CRF - A)

Figure 50: Miscellaneous Combustion Sources/Outlet

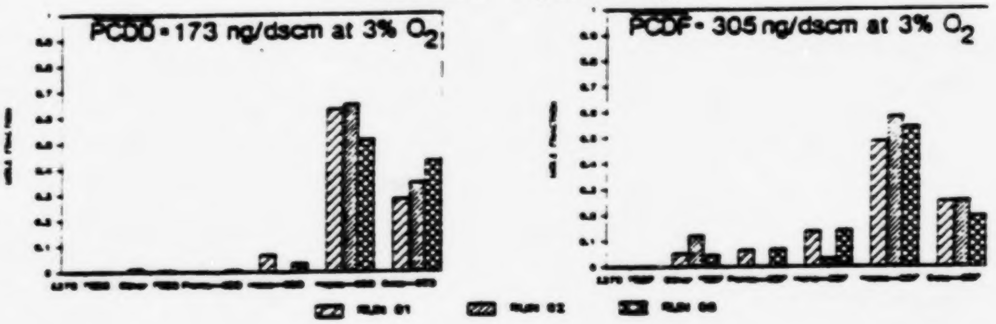
METALS RECOVERY PROCESSES OUTLET

DIOXINS **FURANS**

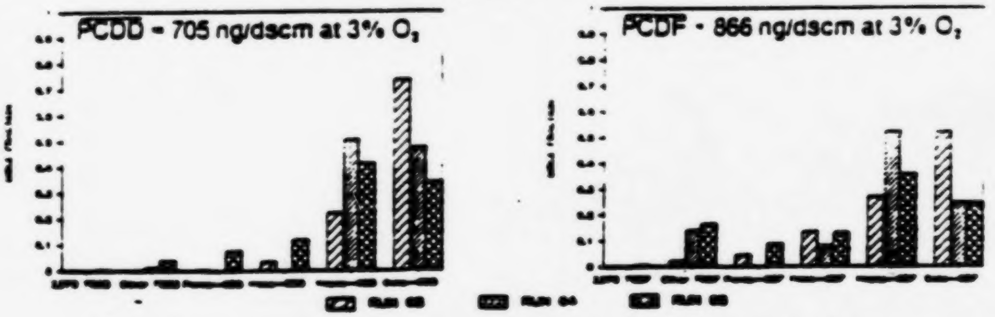
Site MET - A



Site WRI - A (Wire Only)



Site WRI- A (Wire and Transformers)



Dioxin/Furan Homologue Distributions of Controlled Emissions from Metals Recovery Processes (Sites MET - A, WRI - A Wire Only, WRI - A Wire and Transformers)

Figure 51: Metals Recovery Processes/Outlet

Reproduced from best available copy.

REFERENCES

Abenhaim, L., S. Suissa, and D. Bard (1987); Chemosphere **16**, 2129

Addis, G. (1986); Chemosphere **15**, 1265

Asada, S., H. Matsushita, M. Morita, and Y. Hamada (1987);
Chemosphere **16**, 1907

Ballschmiter, K., H. Buchert, R. Niemczyk, A. Munder, and M. Swerev (1986); Chemosphere **15**, 901

Bendixen, E.L. and P.R. Nielsen (1987); Chemosphere **16**, 1943

Benfenati, E. R. Pastorelli, M.G. Castelli, R. Fanelli, A. Carminati, A. Farneti, and M. Lodi (1986); Chemosphere **15**, 557

Bergström, J.G.T. and K. Warman (1987); Production and Characterization of Trace Emissions in Sweden. Waste Management & Research **5**, 395-435

G. Bergvall, J. Hult; Technology, Economics and Environmental Effects of Solid Waste Treatment. Final report from DRAV-project. Publication 85:11, the Swedish Association of Public Cleansing and Solid Waste Management, Malmö, Sweden

Bingham, A.G., C.J. Edmunds, J.J. Gibson, B.W. Graham, and M.T. Jones (1988); Determination of PCDDs and PCDFs in Car Exhaust. Dioxin'88 8th International Symposium on Chlorinated Dioxins and Related Compounds, 21-28 Aug. 1988, Umea, Sweden

Brenner, K.S., I.H. Dorn, and K. Herrmann (1986); Chemosphere **15**, 1193

Brenner, K.S., H. Mader, H. Steverle, G. Heinrich, and H. Womann (1984); Bull. Environ. Contam. Toxicol. **33**, 153

Bröker, G (1987); Maßnahmen zur Verminderung von Dioxinemissionen an Müllverbrennungsanlagen. in: VDI Berichte 634 - Dioxine, pp 515. VDI Verlag, Düsseldorf, 1987

Bumb, R.R., W.B. Crummett, S.S. Artie, J.R. Gledhill, R.H. Hummel, R.O. Kagel, L.L. Lamparski, E.V. Luoma, D.L. Miller, T.J. Nestrick, L.A. Shadoff, R.H. Stehl, and J.S. Woods (1980);
Science **210**, 385

H.-R. Buser (1975); Analysis of Polychlorinated Dibenzo-dioxins and Dibenzofurans in Chlorinated in Chlorinated Phenols by Mass Fragmentography. J. Chromatgr. **107**, 295

Choudhry, G.C. and O. Hutzinger (1983); "Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including PCDD". pp 71. Gordon & Breach, New York - London - Paris - Montreux - Tokyo

Christmann, W., D. Kasiske, K.D, Klöppel, H. Parscht, and W. Rotard (1988); Combustion of Polyvinylchloride - An Important Source for the Formation of PCDD/PCDF. Dioxin'88 8th International Symposium on Chlorinated Dioxins and Related Compounds, 21-28 Aug. 1988, Umea, Sweden

Clement, R.E., H.M. Tosine, and B. Ali (1985); Chemosphere **14**, 815

Clement, R.E., H.M. Tosine, J. Osborne, V. Ozvacic, G. Wong, and S. Thorndyke (1987); Chemosphere **16**, 1895

Cook, R.J. (1987); Solid and Hazardous Waste Incineration: An Analysis for Citizens and Policymakers, Draft, prepared for Toxic Substance Control Commission, State of Michigan

Crummett, W.B. (1982); in "Chlorinated Dioxins and Related Compounds: Impact on the Environment", pp 253. O. Hutzinger, R.W. Frei, E. Merian, and F. Pocchiari, ed.; Pergamon Press, Oxford

Crummett, W.B. and D.I. Townsend (1984); Chemosphere **13**, 777

De Fre, R. (1986); Chemosphere **15**, 1255

des Rosiers, P.E. (1986); The National Dioxin Study. U.S. EPA, Washington, DC

des Rosiers P.E. and A. Lee (1986); Chemosphere **15**, 1313

des Rosiers, P.E. (1987); Chemosphere **16**, 188

Dickson, L.C. and F.W. Karasek (1987); J. Chromatogr. **389**, 127

Dickson, L.C., D. Lenoir, and O. Hutzinger (1988); Surface-Catalyzed Formation of Chlorinated Dibenzodioxins and Dibenzofurans during Incineration. Dioxin'88 8th International Symposium on Chlorinated Dioxins and Related Compounds, 21-28 Aug. 1988, Umea, Sweden

Eadon, G., K. Aldons, D. Hilker, P.O. Keefe, and R. Smith (1983); Chemical Data on Air Samples from the Binghamton State Office Building. Center for Laboratories and Research, New York State Department of Health, Albany, 7 July 1983

Eberhard, H., H. Friege, and E. Schumacher (1986); Müll und Abfall **10**, 377

Eiceman, G.A. and H.O. Rghie (1984); Chemosphere **13**, 1025

Eiceman, G.A., R.E. Clement, and F.W. Karasek (1979); Anal. Chem. **51**, 2324

Eklund,G., J.R. Pederson, and B. Stromberg (1986); Science **320**, 155

Erickson, M.D., C.J. Cole, J.D. Flora, jr.,P.G. Gorman, C.L. Haile, G.D. Hinshaw, F.C. Hopkins, S.E. Swanson, and D.T. Heggem (1985); Chemosphere **14**, 855

Erickson, M.D., S.E. Swanson, T.M. Sack, and D.T. Heggem (1986); Chemosphere **15**, 1261

Fiedler, H. and Hutzinger, O. (1987); Leitstudie - Dioxine; in: VDI Berichte 634, pp. 299, VDI Verlag, Düsseldorf, 1987

Hagenmaier, H., H. Brunner, R. Haag, and M. Kraft (1987a); Environ. Sci. Technol. **21**, 1085

Hagenmaier, H., M. Kraft, H. Brunner, and R. Haag (1987b); Environ. Sci. Technol. **21**, 1080

Haglund, P., K.-E. Egebäck, and B. Jansson (1988); Analysis of PBDD/F in Vehicle Exhaust. Dioxin'88 8th International Symposium on Chlorinated Dioxins and Related Compounds, 21-28 Aug. 1988, Umea, Sweden

Hahn, J.L., H.P. VonDemfange, and C.O. Velzy (1986); Chemosphere **15**, 1239

Hawley-Fedder, R.A., Ph.D.Thesis (1984); Department of Chemistry, Arizona State University

Hay, D.J., A. Finkelstein, R. Klicius, T. Bridle (1987); Chemosphere **16**, 1923

Hileman, F.D., M.D. Hale, T. Mazer, and R.W. Noble (1985); Chemosphere **14**, 601

Hiraoka, M., Y. Takizawa, Y. Masuda, R. Takeshita, K. Yagome, M. Tanaka, Y. Watanabe, and K. Morikawa (1987); Chemosphere **16**, 1901

Hutzinger, O., M.J. Blümich, M.v.d. Berg, and K. Olie (1985); Chemosphere **14**, 581

Hutzinger, O. and H. Fiedler (1987); Sources and Emissions of PCDD/PCDF.
Dioxin'87 7th International Symposium on Chlorinated Dioxins and Related Compounds,
Las Vegas, Oct. 4-9, 1987

Hutzinger, O. and H. Fiedler (1988); Pilot Study on International Information Exchange on Dioxins and Related Compounds, Report Number 173, August 1988. North Atlantic Treaty Organization, Committee on the Challenges of Modern Society

Jansson, B. and G. Sundstrom (1982); in "Chlorinated Dioxins and Related Compounds: Impact of the Environment", pp 253. O. Hutzinger, R.W. Frei, E. Merian, and F. Pocchiari, eds. Pergamon Press, Oxford

Jones, K.H., J. Walsh, and D. Alston (1987); Chemosphere **16**, 2183

Karasek, F.W. and L.C. Dickson (1987); Science **237**, 754

Krishnan S. and R.A. Hites (1980); Chemosphere **9**, 679

Lao, R.C., M. Lanoy, and S.W. Lee, (1983); Polynuclear Aromatic Hydrocarbons, 7th Int. Symp. 1982. Battelle Press

Liberti, A. and D. Brocco (1982); in "Chlorinated Dioxins and Related Compounds: Impact of the Environment", pp 245. O. Hutzinger, R.W. Frei, E. Merian, and F. Pocchiari, eds. Pergamon Press, Oxford

Liberti, A., G. Goretti, and M.V. Russo (1983); Chemosphere **12**, 661

Lindahl, R., C. Rappe, and H.R. Buser (1980); Chemosphere 9, 351

Lustenhouwer, J.K., K. Olie, and O. Hutzinger (1980); Chemosphere **9**, 50

Mahle, N.H. and L.F. Whiting (1980); Chemosphere **9**, 693

Marklund, S., C. Rappe, M. Tysklind, and K.-E. Egeback (1987); Chemosphere **16**, 29

Muller, M.D., and H.-R. Buser (1986); Environ. Sci. Technol. **20**, 1151

National Dioxin Study Tier 4 - Combustion Sources, Project Summary the De-novo Synthesis on Fly Ash of Municipal Waste Incinerators. Presented at Dioxin 87, Las Vegas, Oct. 4-9, 1987 (Chemosphere, in press)

National Dioxin Study Tier 4 - Combustion Sources, Project Summary Report, EPA-45/4-84-014h, United States Environmental Protection Agency (1987)

Nestrick, T.J., L.L. Lamparski, and R.H. Stehl (1979); Anal. Chem. 51, 2273

Nestrick, T.J. and L.L. Lamparski (1982); Anal. Chem. **54**, 2292

Nielsen, K.K., J.T. Moeller, and S. Rasmussen (1986); Chemosphere **15**, 1247

Nilsson, C.A., K. Anderson, C. Rappe, and S.O. Westermark (1974); J. Chromatogr. **96**, 137

Norstrom, A., K. Andersson, and C. Rappe (1977); Chemosphere **6**, 241

Nottrodt, I.A. and K. Ballschmiter (1986); Chemosphere **15**, 1225

Öberg, T., J.-P. Aittola, and J.G.T. Bergström; Chlorinated Aromatics from the Combustion of Hazardous Waste. Chemosphere **14**, 215 (1985)

Olie, K., P.L. Vermeulen, and O. Hutzinger (1977); Chemosphere **6**, 455

Ontario Ministry of the Environment (1985); Scientific Criteria Document for Standard Development, No. 4-84, Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs), prepared for Intergovernmental Relations and Hazardous Contaminants Coordination Branch

Palmer, T.Y. (1976); Nature **263**, 44

Quellmatz, E. (1988); Das neue Chemikaliengesetz - Handbuch der gefährlichen Abfallstoffe. Rechtsstand Juli 1988. WEKA Fachverlage, Kissing; FRG

Rappe, C., S. Marklund, H.R. Buser, and H.P. Bosshardt (1978); Chemosphere **7**, 269

Rappe, C., S. Marklund, L.-O. Kjeller, and M. Tysklind (1986); Chemosphere, **15**, 1213

Reischl, A., Reissinger, M., and Hutzinger, O. (1987); Accumulation of Organic Constituents by Plant Surfaces: Part III; Occurrence and Distribution of Atmospheric Organic Micropollutants in Conifer Needles. Chemosphere **16**, 10 (1987)

Rghie, H.O. and G.A. Eiceman (1985a); Chemosphere **14**, 259

Rghie, H.O. and G.A. Eiceman (1985b); Chemosphere **14**, 167

Sandermann, W., H. Stockmann, and R. Casten (1957); Chem. Ber. **90**, 690

Schecter, A. (1986); Chemosphere **15**, 1273

Sheffield, A. (1985); Chemosphere 14, 811

Southerland, J.H., W.B. Kuykendal, W.H. Lamason II, A. Miles, D.A. Oberacker (1987); Chemosphere **16**, 2161

Steisel, N, R. Morris, and M.J. Clarke (1987); The Impact of the Dioxin Issue on Resource Recovery in the United States. Waste Management & Research **5**, 381

Stieglitz, L. and H. Vogg (1987); Chemosphere **16**, 1917

Stieglitz, L., G. Zwick, J. Beck, W. Roth, and H. Vogg, (1987); On the De Novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators. Dioxin'87 7th International Symposium on Chlorinated Dioxins and Related Compounds, 4-7 Oct. 1987, Las Vegas, U.S.A. (submitted to Chemosphere)

The Hazardous Waste Inspectorate, Hazardous Waste Management: "...Ramshackle & Antediluvian"?, Second Report, Department of the Environment, Welsh Office, Scottish Office, N. Ireland, July 1986

Thoma, H. (1987); PCDD/F-Konzentrationen in Kaminaschen bei Hausfeuerung; in: VDI Berichte 634, pp. 53, VDI Verlag, Düsseldorf, 1987

Thoma, H. (1988a); PCDD/F Concentrations in Chimney Soot from House Heating Systems. Chemosphere **17**, 1369

Thoma, H. (1988b); PCDD/F-Concentrations in Chimney Soot from House Heating Systems. Dioxin '88: 8th International Symposium on Chlorinated Dioxins and Related Compounds, 21-28 Aug. 1988; Umea, Sweden

Tong, H.Y. and F.W. Karasek (1986); Chemosphere **15**, 1219

Tosine, H.M., R.E. Clement, V. Ozvacic, and G. Wong (1985); Chemosphere **14**, 821

Tsuji, M., T. Nakano, and T. Okuno (1987); Chemosphere **16**, 1889

Tysklind, M., S. Marklund, and C. Rappe (1987); Chemosphere **16**, 1937

Vogg, H. and L. Stieglitz (1986); Chemosphere **15**, 1373

Zoller W. and K. Ballschmiter (1986); Fresenius Z. Anal. Chem. **323**, 19